Chapter 4

New Technical Approaches for the Co-processing of Pharmaceutical Wastewater in Municipal Wastewater Treatment Plants in the Shenyang Region

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4.1 Introduction

Hardly any other country has experienced such immense and rapid growth in recent years as the People's Republic of China. In the years 2000–2010, the annual growth rate of the gross domestic product was about 10%; in the last few years (2012–2017), it slowly slowed down to about 7% (World Bank 2015). A major contribution to these rapid developments has been made by the constant growth of industry, which at the same time is leading to much greater environmental problems, including water pollution. The pollution of water resources results mainly from municipal and industrial wastewater discharges. Thus, in addition to unsatisfactory conditions, especially of surface waters, there are often problems in the safe use of these resources for the water supply of the population, industry and agriculture.

The research project SINOWATER- “Good Water Governance Management and innovative technologies to improve water quality in two important Chinese waters” was started in the course of the environmental policy of the Chinese government. With the 11th Chinese five-year plan, which came into force in 2006, concrete targets for improving water quality were set for the first time. In order to achieve the goals set, a water programme, the “National Major Program of Science and Technology for Water Pollution Control and Governance”, was established under the leadership of the Chinese Ministry of Environment and the involvement of six other Chinese ministries of the central government. This programme aims to improve water quality and ecological conditions in large Chinese river basins and lakes, which are to be achieved through mega water projects. The time frame for achieving the objectives has been set for the period between 2006 and 2020. The Federal Ministry of Education and Research (BMBF) concluded an agreement with the Chinese Ministry of Science

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and Technology (MoST) in 2012, which provides for the participation of German partners in the research projects of the mega water projects.

In 2015, the BMBF approved the funding application for the research project SINOWATER- “Good Water Governance Management and innovative technologies for improving water quality in two significant Chinese waters”. The results of the coordination with the responsible persons of two mega water projects led to concentration on one river and one lake catchment area each, namely the Liao River in the province of Liaoning in the northeast of China and the Dianchi Lake near Kunming in the southwest of China.

In the project description for the SINOWATER project the following four main objectives are formulated FIW E.V. [5]:

- 1. “Development of changed structures and organisational measures for improved analysis and decision-making in the normative and operational management of the water sector on the basis of cooperative, participatory and specific ecological research approaches”.
- 2. “Reduction of environmental pollution of water bodies from municipal and industrial wastewater treatment plants”.
- 3. “Participation in the updating of a long-term master plan for Dianchi Lake.”
- 4. “Development of a sustainable concept for sewage sludge disposal in the Shenyang region.

Based on the main objectives, a total of 7 sub-projects are planned under the overall project. Figure 4.1 shows the allocation of the seven sub-projects to the two mega water projects. The whole project is divided into management (M), concept (K) and

Fig. 4.1 Relationship between the Chinese mega water projects and SINOWATER sub-projects

technology projects (T). The two sub-projects T1 and T2 serve to achieve the main objective 2 in the catchment area of the Liao River. In T1, upgrading possibilities for municipal wastewater treatment plants in Shenyang are to be sought in the existing stock in the context of the specific Chinese requirements, whereby the purification line and efficiency are to be optimized by means of process engineering approaches. At T2, new approaches for the combined treatment of municipal and pharmaceutical wastewater are to be developed, which could be applied in the Shenyang region in the future.

In both sub-projects, technology and know-how from Germany will be tested and passed on in China and both sub-projects will be realized by operating a semi-technical MBR pilot plant with additional advanced wastewater treatment stages if required. The importance of the subprojects is to complement the already conducted investigations by Chinese research institutions by the long-term operation of the semi-technical pilot plant and targeted individual and preliminary investigations and to collect meaningful results and experiences in the treatment of municipal and industrial (or pharmaceutical) wastewater with the help of the applied concept under local boundary conditions, which can ultimately contribute to an improvement of the water quality in the catchment area of Liaohé.

4.1.1 New Approaches for the Co-treatment of Municipal and Industrial Wastewater

4.1.2 State of Wastewater Treatment and Upgrading Plan in China and Shenyang

Water is a scarce commodity in China. It is used inefficiently in agriculture, and the discharge of domestic and industrial wastewater and diffuse discharges pollute many of China's water bodies, making them available for only limited use. Due to the increasing pollution of water bodies by a growing population and industry, the demand for better wastewater treatment is also increasing. To address these problems, technical solutions are important, but they will not be sufficient on their own without proper management mechanisms.

4.1.2.1 Administrative Structure and Legal Basis for Wastewater Treatment and Water Protection

Two ministries are responsible for wastewater treatment. The Ministry of Water Resources (MWR, reorganised and renamed as Ministry of Natural Resources as of 03.2018) with its assigned institutes is mainly responsible for the distribution and coordination of water resources and for the protection of water bodies and groundwater. In addition, the Ministry of Environmental Protection (MEP), reorganised

and renamed as Ministry of Ecology and Environment as of 03.2018, issues the laws relevant for wastewater treatment and monitors the implementation of environmental policies. The Ministry of Housing and Urban Rural Development (MOHURD), which is responsible for the construction and maintenance of the infrastructure for water supply and waste disposal, is also responsible. One of the greatest challenges in the Chinese water sector are the complex administrative structures. In particular, the overlapping responsibilities of the various competing actors have been identified as a problem. In addition, areas of responsibility that are not covered by regulations are also proving to be an obstacle.

The first framework law for environmental protection in the People's Republic of China was the "Environmental Protection Law of the People's Republic of China". The "Law of the People's Republic of China on the Prevention and Control of Water Pollution" details this law in the field of water management. In terms of implementation, the Implementing Rules on the Law on the Prevention and Control of Water Pollution and the Regulations on Issues concerning experimental collection of urban sewage treatment fee are valid. Further regulations exist at provincial level. Parallel to the laws mentioned, standards must be observed which are issued by the central government/ministry in Beijing, but also by the provincial governments. The relevant state standards for wastewater management are listed in Table 4.1.

The effluent concentrations of municipal sewage treatment plants are prescribed by law GB 18,918–2002, similar to the German law GB 18,918–2002. In contrast to Germany, where a certain concentration in the effluent of the sewage treatment plant may not be exceeded depending on the size class, Chinese sewage treatment plants are divided into three standard classes based on the effluent concentration, irrespective of their size class. Table 4.2 shows the effluent concentrations of the Chinese standard classes (SK) with the effluent concentration of "size class 5" (GK) according to the German Wastewater Ordinance. It can be seen that the highest Chinese standard class IA is considerably stricter than the German one.

The definition of the discharge standard is strongly dependent on the water body to be discharged. Depending on the quality category, immission values for surface waters are similarly specified in GB 3838–2002. If sensitive waters or water resource protection areas are involved, higher discharge standards must be achieved. In many priority regions, the state discharge standard is therefore tightened to varying degrees

Table 4.1 Environmental and quality standards relevant to water and wastewater in the People's Republic of China

Title of the standard	Number
Quality standard surface water	GB 3838—2002
Discharge standard of waste water into municipal sewers	CJ 3082—1999
Emission standard from municipal sewage treatment plants	GB 18918—2002

Table 4.2 Parameters in the inflow of the pilot plant

Parameters	Unit	GK 5 (>6000 kg _{SSB5} /d)	SK I		SK II	SK III
			A	B		
COD	mg/l	75	50	60	100	120
BOD₅	mg/l	15	10	20	30	60
SS	mg/l	-	10	20	30	50
Animal/vegetable fat	mg/l	-	1	3	5	20
Crude oil or similar	mg/l	-	1	3	5	15
Surface active substances LAS	mg/l	-	0,5	1	2	5
N_{ges}	mg/l	13	15	20	-	-
NH₄-N	mg/l	10	5	8	25	-
P_{ges} (Commissioning before 31.12.2005)	mg/l	1	1/0,5	1,5/1	3	5
P_{ges} (Commissioning after 31.12.2005)	mg/l	1	0,5	1	3	5
Colouring	-	-	30	30	40	50
pH	-	-	6–9	6–9	6–9	6–9
Faecal colony count	/l	-	1.000	10.000	10.000	-

in order to increase the purification capacity of wastewater treatment plants, reduce the discharged pollution loads and thus improve water quality.

4.1.2.1.1 Institutions, Procedures and Challenges

In 2010, a total of 62 billion m³ of wastewater was produced in China. By 2015, the volume of wastewater had increased to 73.5 billion m³ with approximately 20 billion m³ of industrial wastewater and 53.5 billion m³ of domestic wastewater MEP [12] and [13].

Similarly, the number of municipal wastewater treatment plants increased from about 2800 in 2010 to over 6000 plants in 2015 according to the annual statistical report of the Ministry of Ecology and Environment, which, with a total capacity of 53.2 billion m³/d, were able to treat a total of about 9 billion m³/d of wastewater in 2015, more than in 2010. The treatment capacity corresponds to a connection rate of about 73%. Depending on their capacity, the treatment plants are allocated to the following size categories on a percentage basis, in proportion to the total number Jin et al. [8].

- 9% Small sewage treatment plants with capacities up to 10,000 m³/d:
- 75% Medium-sized sewage treatment plants with a capacity of 10,000 to 100,000 m³/d
- 16% Large wastewater treatment plants with a capacity exceeding 100 000 m³/d

In most cases, similar concentrations of wastewater parameters are present in municipal wastewater as in Germany. Due to leaky sewers and the resulting infiltration of extraneous water, however, very low concentrations of COD and BOD₅ in

wastewater were found in the greater Shanghai area, Kunming and many regions of northern China Yun [25].

From a technical point of view, most municipal wastewater treatment plants in China currently consist of a mechanical treatment stage, primary treatment, biological treatment stage or secondary treatment. Since the introduction of different minimum standards in 2002, investments in the field of wastewater treatment have increased rapidly. The aim was to reduce the content of nitrogen and phosphorus in wastewater. Especially for industrial wastewater, the AAO treatment process, an effective, relatively inexpensive and easy to implement treatment option, is used.

The Urban Water Environmental Department of CRAES Tian [22] published a China-wide overview of 828 wastewater treatment plants with a total wastewater treatment capacity of about 63 million m³/day (Fig. 4.2). Of the wastewater treatment plants, 2% have only a basic treatment stage, 89% have a mechanical–biological treatment stage and 9% have an additional more advanced treatment stage. The biological stages use the AAO and AO process as the most common technique, followed by aeration ditches and SBR systems. As further techniques the main biofilm processes are used. Process combinations such as SBR, ABR, UASB and CASS are also used to improve the purification performance. All larger (from 100,000 m³/d) sewage treatment plants have a disinfection stage (UV radiation or chlorination) installed in the effluent to disinfect the treated wastewater.

Despite the existing modern wastewater treatment processes, the actual purification performance of many wastewater treatment plants in China is unsatisfactory. Several reasons for this have been identified:

- complex wastewater composition and unclear discharge source
- low operating temperature in winter
- incomplete monitoring and sampling
- backlogged procedures or investment and energy restrictions

Fig. 4.2 Treatment techniques

- unsafe sludge disposal
- unqualified wastewater specialists and poor operation

For this reason, the Chinese experts attach great importance to upgrading the systems, which is also the aim of T1. Some of the sewage treatment plants are located in densely populated or rapidly developing areas, so that only small areas are available for a sewage treatment plant expansion. Necessary increases in capacity or more extensive purification services therefore generally require an area-neutral optimisation of the sewage treatment plants.

Apart from a few exceptions, most wastewater treatment plants in China use simultaneous aerobic sludge stabilization during biological wastewater treatment. Energy optimization measures such as power generation by sludge digestion are difficult to realize due to several limitations. There are also no plans for the elimination of micropollutants discussed in Germany. In addition, the focus of wastewater disposal in China has so far been on wastewater treatment. This means, however, especially in the case of heavy rainfall events, considerable material pollution of the surface waters through wastewater discharges or wastewater relief. Checking the condition of sewers and optimising the upstream sewerage system are therefore also possible upgrading measures in China Yun [25].

4.1.2.1.2 Environmental Problem and State of Wastewater Treatment in Shenyang

As one of the two study areas, Shenyang is located in the northeast of the People's Republic of China and is the capital of Liaoning Province. Benefiting from government support, Shenyang is an economic and cultural center in the northeast of the country.

Shenyang is located in the floodplain of the Liao and Hun rivers on the southern edge of the northeast China plain. The terrain slopes gently from northeast to southwest. Shenyang has a continental climate characterized by hot, humid summers due to the monsoon and dry, cold and extremely long winters due to the Siberian high pressure system. The average annual temperature in Shenyang is 8.3 °C. The average temperatures are 25 °C in July at the warmest time and about −15 °C in January at the coldest time. Extreme temperatures range from below −30 °C Meteoblue AG [14]. In January 2018, the SINOWATER pilot plant, which was located on the site of the reference wastewater treatment plant in Shenyang, experienced a daytime low temperature of −33 °C. About 500–600 mm of precipitation falls on average within one year and most of the annual precipitation occurs from June to September.

The city of Shenyang has a total area of about 12,860 km² and is composed of ten urban districts, two counties and one independent city. The population in 2015 was about 7,300,000 in the metropolitan region. The average population density of the Shenyang metropolitan region is 568 inhabitants/km².

The city is known as the “Ruhr Area of the Orient”, and since the beginning of the twentieth century has been the economic centre for the whole of north-eastern China and the headquarters of the Chinese manufacturing industry. Similar to its German counterpart, Shenyang has a long history as an important industrial center in northeast

China and is today a location for the automotive, mechanical engineering, chemical, pharmaceutical and financial industries. Due to various problems concerning the technical state of the art, the organizational structure, the environmental pollution as well as the unfavorable climatic conditions of urban design, the whole region of Northeast China is subject to a slowly decreasing economic growth at the beginning of the Chinese reform and opening policy in 1978. In the 1980s and 1990s, many reconstruction measures were therefore carried out in the old Tiexi industrial district in Shenyang, which is one of the largest and most heavily used urban industrial areas in China. In 2002, a new land use plan for the city of Shenyang was presented, according to which many industrial factories were to be moved from the urban core area to new industrial and economic development zones further west Zhang [26]. This relocation was part of a new urban design to accommodate economic shifts in Shenyang. In view of various factors, Shenyang has become increasingly attractive since the 1990s and is attracting the interest of global corporations as well as German small and medium-sized enterprises. One of the city's most advanced projects in the new industrial zones today is the Chinese-German "Intelligent Equipment Manufacturing Industrial Park", another example of the regional administration's efforts not only to promote Shenyang in its role as the world's largest center of machine tool manufacturing, but also to encourage international companies to set up operations in the vicinity of their customers.

In Shenyang, natural and industrial influences result in special requirements for the protection of regional water resources, especially the Liao River in Liaoning Province, which is the largest river in northeast China with a length of 1390 km. As a conventional heavy industrial city in the catchment area of the Liao River, the city of Shenyang has long been seriously confronted with environmental problems, especially the issue of wastewater treatment. The already explained fact that almost 80% of the annual precipitation falls between June and September means that for many months very little runoff is discharged into the surface waters of the catchment area. Especially in the densely populated metropolitan region of Shenyang with over 7 million inhabitants and the numerous industrial enterprises, the large wastewater pipes cause high concentrations of pollutants in the surface waters there. In the catchment area of the Liao River, this particularly affects the tributary Hun and its tributaries Xi, Pu, Baitapu and Mantung.

The Hun River flowing through Shenyang is highly polluted by industry. For example, in 2013, NH₄-N and TP concentrations exceeded the minimum requirements of the highest water quality class in China in all tributaries of the Hun River. The high level of pollution can be explained by the many industrial plants, the large population and the low water volume. According to CRAES, pharmaceutical wastewater and agricultural wastewater are the main sources of NH₄-N pollution.

The first sewage treatment plant Beibu was built in Shenyang in 1994, and between 2002 and 2007 the first significant expansion of the capacity of the sewage treatment plant took place. Towards 2010, the last large treatment plant and several small treatment plants were built along the Pu River, so that almost all the wastewater from the city districts can be treated and the connection rate has now reached 95%. Since

then, industrial wastewater is completely discharged into the sewage treatment plants Shenyang EPB [21].

Figure 4.3 shows the development of the treatment volume of the municipal wastewater treatment plants in the Shenyang urban region since 2004. 2016 about 731 million m³ of wastewater were treated in Shenyang, i.e. about 2 million m³/d, which was three and a half times the amount of 2004 Hu [6] and Shan [20].

There are currently 37 wastewater treatment plants with a total capacity of 2.8 million m³ of wastewater per day: Shan [20].

- 7 sewage treatment plants with >100.000 m³/d
- 6 sewage treatment plants with 50.000–100.000 m³/d
- 25 sewage treatment plants with <50.000 m³/d

It should be noted that municipal wastewater treatment plants are mainly located in the core area of the city. In contrast, the more rural districts together have only a few treatment plants.

Altogether, 83.2% of the wastewater generated in Shenyang is treated, while the average capacity utilisation of the treatment plants is 71.4%. This means that about 405,000 tons of wastewater (presumably industrial and municipal wastewater as well as outdoor discharges) are discharged untreated into the waters in and around Shenyang every day. According to official requirements of the local environmental authority, 28 of the 37 sewage treatment plants have to comply with the minimum effluent concentrations of SC I from the time of commissioning, while the effluent values of the other 9 plants should correspond to SC II. Table 4.3 gives an overview of the number and capacity of the treatment plants depending on the standard classes to be met in Shenyang.

It is clear from this that the 21 treatment plants, which are supposed to comply with effluent concentrations of SK IA, treat only 0.79 million m³ in total and are not sufficiently utilised. The reason for this is that some of them have not yet been commissioned or are currently undergoing conversion/expansion with the purpose of upgrading. In category SK II there are many large treatment plants with a total

Fig. 4.3 Development of the annual treated wastewater volume in the urban region of Shenyang

Table 4.3 Distribution of municipal wastewater treatment plants and treatment capacity in Shenyang according to Shan [20]

	SK I A	SK I B	SK II
Quantity	21	7	9
Design capacity	1,44 Mio. m ³	0,17 Mio. m ³	1,25 Mio. m ³
actually treated waste water quantity in 2016	0,79 Mio. m ³	0,09 Mio. m ³	1,12 Mio. m ³

throughput of 1.12 million m³ of wastewater, which corresponds to more than 50% of the total wastewater volume Shan [20].

Therefore, unfavourable inlet compositions and missing requirements for process selection and operation are responsible for the effluent concentration of SK II. This leads to an insufficient elimination of pollutants in the wastewater treatment plants. An unpublished study report by the Shenyang Academy of Environmental Sciences shows that the effluent values of nutrient parameters such as TN, NH₄-N and TP exceed the limits of the respective classes in many wastewater treatment plants.

Starting in 2018, the environmental authority has set the effluent concentrations of SK IA as binding for the sewage treatment plants in Shenyang. There is therefore a great need for upgrading the old treatment plants, which account for over 50% of the total treatment capacity in Shenyang and cannot meet modern discharge standard requirements in the long term due to the high inflow values. In addition, the city is also making efforts to develop new management measures and technical approaches for the treatment of specific industrial wastewater streams, such as the co-treatment of pharmaceutical wastewater in municipal wastewater treatment plants. These are also reasons for the implementation of the two SINOWATER subprojects T1 and T2.

4.1.2.1.3 Status of Pharmaceutical wastewater Treatment in China and the Pharmaceutical Company “Northeast Pharmaceutical Group Co, Ltd. in Shenyang

China is regarded as the world’s largest manufacturer of raw pharmaceuticals and stands out due to the size of the country and its large population with large quantities of pharmaceuticals consumed. The pharmaceutical industry accounts for 1.7% of the gross domestic product of total industrial production in China. In the manufacture of pharmaceuticals, the consumption of raw materials is between 10 and 200 kg per kilogram of active ingredient produced. This process produces a lot of heavily polluted pharmaceutical wastewater (PA), so that 2% of the total wastewater volume in China is attributable to the pharmaceutical industry (Xiao and Zhang [24] Zeng et al. [27]).

In China, PA has a complex composition and contains a large number of organic pollutants in high concentrations. The most important of these are COD, BOD₅, NH₄-N, SS and dyes (including turbidity caused by toxic ingredients). It is also characterised by strongly varying pH values and high salt contents. The amount and composition of wastewater is subject to strong fluctuations Xiang [23].

The circumstances described above call for an improvement or targeted expansion of wastewater treatment systems in Chinese industry. Some of the procedures already applied in the Chinese pharmaceutical industry are described below: Li and Li [11].

Physical–chemical treatment processes:

- Coagulation as the most economical sedimentation process, which not only reduces the concentration of pollutants in the wastewater, but also increases biodegradability.
- Flotation: impurities adhere to gas bubbles, which rise to the surface and can be separated.
- Adsorption processes in which drug residues, but also the COD, the colour and the odour are adsorbed by adsorption effects on e.g. coal.
- Fenton method: In acidic medium, organic substrates are catalysed with hydrogen peroxide by iron salts. In the wastewater treatment plant of a pharmaceutical company in Wuhan, a COD elimination level of over 90% can be achieved by using this process.

Biological treatment processes:

- Aerobic processes: Various aerobic processes are used in the wastewater treatment plants of Chinese pharmaceutical companies: Sequencing Batch Reactor (SBR), Cyc-lic Activated Sludge System (CASS), Cyclic Activated Sludge Technology (CAST), Intermittent Cycle Extended Aeration System (ICEAS), Modified Sequencing Batch Reactor (MSBR) etc.
- Anaerobic process: In China, anaerobic fermentation is currently used as the main approach for anaerobic processes, as it offers several advantages: high organic load degradable, low OEL production, simple sewage sludge dewatering, no aeration required, recovery of biogas possible.
- Combination of aerobic and anaerobic processes: In order to exploit the advantages of both processes, they are often combined. The following combinations are often used in the Chinese pharmaceutical industry: Microelectrolysis - anaerobic hydrolysis and acidification process - SBR; pretreatment - Upflow Blanket Filter (UBF) - contact oxidation - Biological Aerated Filter (BAF); hydrolysis and acidification process - Upflow Anaerobic Sludge Blanket (UASB) - SBR. The wastewater treatment plant of the pharmaceutical company “Northeast Pharmaceutical Group Co., Ltd.

Furthermore, there are other strategies to reduce the negative environmental impact of the pharmaceutical industry in China. These are the implementation of new management systems, clean production facilities in terms of water consumption and pollution, deeper quality control, new management strategies in the companies and the government, and the investigation and application of new processes for pre-treatment, biochemical treatment and advanced wastewater treatment of the wastewater generated by the pharmaceutical industry.

In Germany, the topic of the 4th purification stage or elimination of trace substances has been discussed for several years. As in Germany, Chinese waters

are also polluted by the pharmaceutical industry and by the consumption of pharmaceuticals through pharmaceutical trace substances, which have negative effects on flora and fauna. It is important to identify the pathways of entry and to prevent the entry. Furthermore, controls must remain strict in order to prevent the illegal discharge of polluted wastewater. The aim of wastewater treatment in the pharmaceutical industry should be the elimination of typical wastewater parameters as well as the elimination of trace substances.

As mentioned above, the SINOWATER pilot plant for sub-project T1 with municipal wastewater for T2 was fed with a mixture of municipal and pharmaceutical wastewater. The PA is the water from the effluent of the wastewater treatment plant of the pharmaceutical company “Northeast Pharmaceutical Group Co. Ltd. (NEPG)”, founded in 1946, is one of the largest companies in the field of chemical synthesis and bio-logical fermentation. In addition, the company’s business activities include Western medicine preparation and micro-ecological preparation as well as the distribution of pharmaceutical products. NEPG produces 12 large series of active ingredients including vitamin series, antibiotics, anti-AIDS drugs, digestive drugs, narcotics and cardiovascular and cerebrovascular drugs. The company owns the largest production line for vitamin C in the world and the independent technical property right for purely chemical synthesis of berberine. The company also has a processing base for feed additives and veterinary drugs based on pharmaceutical raw materials NEPG [17].

Information on the NEPG’s treatment plant and the quality of the wastewater on site was obtained during visits to the pharmaceutical plant and discussions with the contact persons. Figure 4.4 shows a diagram of the company’s wastewater treatment plant, which is located on the NEPG site in Shenyang. The two partial water flows A and B together have a volume flow of 6,000 to 7,000 m³/day. Due to the high inflow values of the heavily polluted wastewater, this partial flow passes through two complete cleaning cycles. Table 4.4 lists the parameters COD, BOD₅, pH and SS of the two partial flows in the feed.

Fig. 4.4 Flow chart of the wastewater treatment plant “Northeast Pharmaceutical Group Co., Ltd

Before the streams are subjected to hydrolysis and acidification, they pass into regulation basins, where various substances can be dosed. The pH value can also be adjusted there. In the anaerobic basin, hydrolysis and acidification take place. The pre-treated wastewater is then transferred to the aeration tanks. The treatment plant has a large number of aeration tanks, as the biological treatment works according to the SBR principle. This means that the sludge is not separated from the purified wastewater in an external secondary clarifier by settling, but the settling process is waited for in the activation tank and the supernatant is then pumped out. There are always basins in different phases of the batch operation, so that a continuous wastewater treatment can take place. The remaining sludge is partly pumped back into the inlet of the activation as return sludge. The rest is discharged in the form of excess sludge.

After the biological treatment of the heavily polluted wastewater, this water undergoes the same purification process - from hydrolysis and acidification - together with partial stream B once again. The aeration tanks in the second purification line of the wastewater treatment plant also operate in batch mode (SBR). In contrast to the first cleaning line, it is possible to dose PAH into the aeration tanks.

In the diagram two possible paths of biologically treated wastewater are shown after the activation tanks of the second treatment line. At the beginning of the project (November 2017 to the beginning of January 2018), the water did not undergo any additional treatment, but was discharged into the municipal sewage system. From mid-January onwards, NEPG put an external membrane stage into operation. A PTFE membrane manufactured in Japan is used in the form of a capillary module, which is constructed from tubular membranes.

The discharge of the NEPG WWTP into municipal sewers is done as described in Chapter 2.1.1 and Table 4.1 explains the administrative structure and legal basis for wastewater treatment and water protection according to the national discharge standard CJ 3082–1999 for indirect dischargers. Officially, however, the treatment plant has to comply with the regional discharge standard DB 21/1627–2008 for Liaoning Province, which was issued in 2008 and is stricter than the state standard. The prescribed minimum discharge values of some main sum parameters are shown in the following table. The actual effluent quality of the NEPG treatment plant (as part of the inlet to the SINOWATER pilot plant) during the operation phase for T2 is described in detail in chapter 2.4 due to its complexity.

The pharmaceutical wastewater treated in this way was to be discharged through a separate sewer to a treatment plant, which was newly built in 2016 and has a

Table 4.4 Parameters of the partial water flows A and B of the NEPG wastewater treatment plant

Partial flow	COD (mg/L)	BOD ₅ (mg/L)	pH	SS (mg/L)
A: heavily polluted wastewater	10.000 – 20.000	3.000 – 8.000	6 – 9	~500
B: slightly polluted wastewater	~1.000	300 – 400	6 – 9	~200

Table 4.5 Minimum requirement of main sum parameters in the national and regional discharge standard into municipal sewer systems (with treatment plant at the end)

Parameters	Unit	national initiation standard CJ 3082—1999	regional induction standard DB 21/1627-2008 (Province Liaoning)
COD	mg/l	500	450/300
BOD₅	mg/l	300	250
SS	mg/l	400	300
N_{ges}	mg/l	-	50
NH₄-N	mg/l	35	30
Phosphates	mg/l	8	5

Table 4.6 Membrane type and TMP of membrane processes Pinnekamp and Friedrich [19]

Membrane processes	pore size	Membrane type	TMP	Operating mode
Microfiltration	0,1 - 5 μm	Pore-membrane	0,1 – 3 bar	Crossflow- u. Dead-End-Betrieb
Ultrafiltration	0,005 - 0,1 μm	Pore-membrane	0,5 – 10 bar	Crossflow- u. Dead-End-Betrieb
Nanofiltration	0,001 – 0,01 μm	LD-membrane	2 - 40 bar	Crossflow-Betrieb
Reverse osmosis	< 0,001 μm	LD-membrane	5 – 70 bar	Crossflow-Betrieb

daily treatment capacity of approx. 250,000 m³ of wastewater, consisting of approx. 7,000 m³ of pharmaceutical wastewater and 180,000 municipal wastewater. Due to the possibility of treating both wastewater streams simultaneously, this treatment plant was selected as the site for the pilot plant at the beginning of the project. However, due to the lack of a sewerage system and an unresolved operating permit, the treatment plant could only be put into operation from the end of 2017 onwards with highly contaminated industrial wastewater, which caused the relocation of the test plant according to “GWSTP”.

4.1.2.1.4 Parallel Research Activities

According to experience, the pre-treated pharmaceutical wastewater as well as the industrial wastewater in Shenyang is generally characterized by poor biodegradability (e.g. unfavorable B/C or C/N ratio), which is a great challenge for the downstream treatment plant with high requirements on effluent concentrations. Therefore, in the past years in Shenyang different considerations for further treatment measures were made and corresponding laboratory tests were carried out. These concerned.

- Adsorption of the hardly degradable components of pharmaceutical wastewater to the biological sludge of a municipal sewage treatment plant
- the ozonation of the pharmaceutical wastewater to break down the refractory substances and
- the hydrolysis and pre-acidification of pharmaceutical wastewater to increase the degradability

Table 4.7 Division of the total project period on site into operational phases

Period		Part-project	Operating phase/ Test series	Purposes
2017	week 19-21	T1+T2	Structure and Commissioning	-
	week 22-26	-	Test phase	Test operation phase with highly polluted industrial wastewater as inflow due to local restrictions
	week 29-30	T1+T2	Relocation and New structure	-
	week 31-39	T1+T2	Run-in phase MBR	Concentration of the activated sludge and adjustment of the inlet to a sufficient return ratio within the plant
	week 40-44	T1	MBR (+GAK) ¹	Control and documentation of the cleaning performance, the membrane and sludge parameters, as well as the discharge after the GAK filter
	week 45-47		MBR + C-Quelle (+GAK)	Test phase to improve the cleaning performance of the test plant by adding an external C source
	week 47-49	T2	MBR + GAK	Adjustment of the feed of PA until the desired mixing ratio of 28% is achieved
2017/ 2018	week 50; 4		MBR + Postozoning + GAK	Test phase for the investigation of the cleaning line of different combinations of the cleaning stages
	week 51; 5		Preozoning + MBR + GAK	
	week 52 — 2		FM/FHM + MBR (+PAK) ² (+ GAK)	
	week 6-7		MBR + PAK (+ GAK)	
2018	week 3	T1	FM + MBR	Supplementary test phase for T1 due to an operational failure of NEPG
	week 8	T1	MBR + PAK (+GAK)	Additional test phase for T1 due to the breakdown of NEPG
	week 9 - 10	T2	MBR (+GAK)	Additional test series with increased PA content of up to 100%
	week 11-12	T1+T2	Decommissioning	-

¹The filtrate must always pass through the activated carbon filter before being discharged

²Passive dosing of PAH due to the massively changed feed quality

The combination of sludge adsorption and ozonation proved to be most promising. Figure 4.5 shows the first positive results of the investigations. The BOD5/COD ratio could also be increased from 0.1 to about 0.3 by ozonation. In 2015, a corresponding semi-technical pilot plant was operated by the Chinese cooperation partner at a municipal wastewater treatment plant in Shenyang, where the process combination of sludge adsorption and ozonation is seen as a pretreatment step prior to co-processing in a municipal modified AAO reactor (Fig. 4.6). However, the investigations have shown that with the desired quantity ratio of pharmaceutical wastewater (approx. 30%), the required COD effluent values of standard class IA of 50 mg/l could not be met despite the pretreatment combination (Fig. 4.7) Xiang [23].

Discussions with the Chinese side revealed that no studies have been conducted to date on adsorption on activated carbon. Thus, the process engineering solution envisaged in subproject T2 was developed, which is also regarded by the Chinese side as a promising alternative to the previous solution options. The effect of the

Table 4.8 Overview of sampling points and sampling

Extraction point	Type of sample	Statement	Parameters
Reservoir of GWSTP	composite sample	Feed concentration KA	COD, BOD ₅ , NH ₄ -N, TN, TP, SS
Tanker truck/ Reservoir	sample	Feed concentration PA	COD, BOD ₅ , NH ₄ -N, TN, TP, NO ₂ -N, NO ₃ -N, SS
Ball valve of the coarse material cell	sample	Control of operating sequence	COD
Ball valve of the nitrification tank	sample	Waste water and sludge parameters	SV30, TS, (COD)
Ball valve of the filter chamber	sample	sludge parameters r	SV30, TS
Ball valve of the filtrate pump	composite sample	Outlet concentration MBR	COD, BOD ₅ , NH ₄ -N, TN, TP, SS, (NO ₂ -N, NO ₃ -N) ³
Ball valve of the filtrate tank	composite sample	Outlet concentration/ Post-ozoning procedure	COD, BOD ₅ , NH ₄ -N, TN, TP, SS
Drain hose of the test facility	sample	Outlet concentration after GAK filter	COD, (TN, TP)

³NO₂-N and NO₃-N were only determined during test phase T2 due to local restrictions

Fig. 4.5 Test results for the adsorption on activated sludge of a municipal wastewater treatment plant (left) and for the ozone oxidation (right) of pharmaceutical wastewater in Shenyang

activated carbon is to be enhanced by the use of a membrane separation stage. In this way, it will be possible to keep the sludge concentration in the activated sludge tank three to four times higher than in other sludge concentrations in order to achieve improved decomposition of the refractory materials (Fig. 4.5).

- Example sludge adsorption: MLSS 1 g/L, T = 15 min., COD Elim. = 33%, BOD/COD = 0,11
- Example ozonisation: Dosiermenge 20 mg/L, T = 30 min., COD-Elim. 0 42%, BOD/COD = 0,31

Fig. 4.6 Chinese modified AAO pilot plant for combined treatment of municipal and pharmaceutical wastewater in Shenyang (FiW)

Fig. 4.7 COD-related operating results of the pilot plant with 30% pharmaceutical wastewater

4.1.2.2 Innovative Membrane Technology in wastewater Treatment and the Pilot MBR-Treatment Facility in Shenyang

4.1.2.2.1 Membrane Filtration in Wastewater Treatment

Membranes work according to the principle of a filter. They are used for the separation of substances and, depending on the membrane and the process, can separate wastewater components up to a molecular size. The wastewater to be treated is also called “feed” and is separated by the membrane into two phases: the clear effluent as filtrate (or permeate) and the filtered out contaminants as concentrate (or retentate). The morphology is idealised by distinguishing between pore and solution diffusion membranes (LD membrane), so-called dense membranes Baumgarten [1]. Depending on the separation limit (pore size of the membrane), membrane filtration

can be further subdivided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The driving force for the mentioned separation processes is the pressure difference between feed and permeate side, the so-called transmembrane pressure difference or transmembrane pressure (TMP). The TMP increases with decreasing separation limit of the membranes used. A summary of the pore size, membrane types or typical TMP and operating mode of the different membrane processes can be found here (Table 4.6).

In municipal wastewater treatment, micro- or ultrafiltration membranes with a pore size of up to 0.1 μm are often used, where almost complete retention of all kinds of bacteria and most viruses could be achieved, while the processes to be applied in industrial wastewater treatment can extend to reverse osmosis due to the requirement to treat highly contaminated wastewater.

In addition to the separation limit, membrane processes can also be distinguished by their design, materials and operating modes. For membranes, a distinction can be made between the two basic forms of flat membranes and tubular membranes. The membranes are arranged in modules. In addition to the membrane, the arrangement and choice of module plays a major role in the cleaning performance of a membrane stage. Since membrane modules are designed depending on the intended use, there is a large number of different module designs. For example, tubular membranes can be used to form tubular modules, capillary modules or hollow fibre modules. Wound modules, cushion modules, disc-tube modules or plate modules are some module forms in which flat membranes are installed Pinnekamp and Friedrich [19].

Both organic and inorganic materials could be used. Organic or polymeric membranes are dominant in all membrane processes (MF, UF, NF, RO) in wastewater treatment. The reasons for this are the lower production costs compared to inorganic membranes and the possibility to select the most suitable polymer for a specific separation problem from the large number of existing materials. Common materials for MF and UF are e.g. polysulfone (PS), polyethersulfone (PES), polypropylene (PP) and polytetrafluoroethylene (PTFE). Inorganic materials, such as ceramics, aluminium and stainless steel, are also mainly used in the MF and UF sector. Advantages over organic membranes are mainly in the mechanical, chemical and thermal resistance Baumgarten [1].

Basically, the two usual operating modes cross-flow operation and dead-end operation dominate, whereby the difference lies in the angle of incidence of the wastewater flow to be treated to the membrane surface. In cross-flow operation, the membrane is exposed to a transverse flow, whereas in dead-end operation the membrane is exposed to the feed vertically Pinnekamp and Friedrich [19].

The membrane bioreactor process (also known as membrane bioreactor process) is the combination of an aeration tank and a membrane filtration. In this process, the membrane stage replaces the secondary settling tank to separate the biologically purified water (filtrate) from the biomass (concentrate). Here, a distinction can be made between two variants:

- Internal membrane stage: membrane module placed in aeration tanks
- External membrane stage: separately installed membrane module outside the aeration tank

In Fig. 4.8 the two mentioned variants of the membrane bioreactor process are schematically shown. If a membrane stage is connected downstream of a biological treatment stage, the aim is to achieve complete solids retention and an extensive hygienisation of the effluent Pinnekamp and Friedrich [19].

In this process, the activated sludge, including all microorganisms, is completely retained by membranes. During operation, the so-called filter cake grows on the membrane surface, which can lead to the formation of a cover layer and must be removed after a certain time in order to prevent permanent blocking of the membrane pores. In all operating modes, the membranes must therefore be back-flushed with air or water (usually by cross-flow aeration). In addition, the effects mentioned below can also lead to a decrease in filtration performance Baumgarten [1]:

- Biofouling: Biofilm formation on the membrane surface
- Colloidal fouling: Accumulation of colloidal (finely divided) dissolved substances leads to a kind of film or slime on the membrane surface
- Scaling: deposits on the membrane formed by crystallization (precipitation)

In the last decades, the membrane bioreactor process has gained more and more importance in wastewater treatment. The advantages of the membrane bioreactor process result from the higher solids content in the aeration tank and the complete retention of particles, microplastics, bacteria and germs by the membranes (and possibly viruses), so that secondary clarification, sand filtration and UV disinfection are not necessary. An improved elimination of organic trace substances can also be enumerated Pinnekamp and Friedrich [19].

The biological stage of membrane bioreactors is designed according to the sludge age, whereby the design sludge age is in the usual range of conventional activated sludge plants. Thus the volume of the activated sludge tank can be dimensioned according to ATV Worksheet 131 (2000), whereby a higher solids content of about 10 to 15 g/L must be assumed. MBR plants can be combined with the usual processes for carbon and nitrogen elimination and for simultaneous aerobic sludge stabilization without any restrictions Krause et al. [4] DWA-M 22738 [10]. The specific

Fig. 4.8 Membrane activated sludge process according to Pinnekamp and Friedrich [19]

excess sludge generation corresponds to that of conventional plants. The municipal membrane bioreactor plants in Germany are currently operated with a sludge age of more than 25 days. The reason for this high sludge age is the lower fouling potential that can be expected Itokawa et al. [7] Judd [9].

The design of the membrane filtration stage depends on the maximum inflow or the area-specific flow for the membrane modules. Decisive design parameters for this are usually the permeability, which for new or cleaned membranes should normally be in the range 150–200 l/(m²-h-bar) and for intensive cleaning <100 l/(m²-h-bar), or the membrane flow, which can vary from 5 to a maximum of 25–30 l/(m²-h) Pinnekamp and Friedrich [19].

In the MBR, which was used during the project, an internal membrane stage in the form of a plate module was installed with a sludge age of more than 20 days in the entire bioreactor.

4.1.2.2.2 Experimental Installation: Design, Construction and Operation

The pilot plant used in Shenyang is a membrane bioreactor with different pre- and post-treatment options. As already mentioned, the entire pilot plant was built as an integrated container wastewater treatment plant (or ship treatment plant) by the German industrial partner MMS in Germany and shipped to the site in China. The process flow is shown schematically in Fig. 4.9 with the construction units. The blue dotted border marks the outer walls of the test plant or container. Dosing equipment and all further cleaning stages are outlined with red dotted lines and were subsequently installed in the test plant on site at the project location in China. The blue turned squares in Fig. 4.9 indicate possible sampling points. The whole system consists of:

Fig. 4.9 Schematic layout of the SINOWATER pilot plant

- a flocculation plant for the pre-treatment of the raw wastewater,
- a mechanical pre-cleaning unit for the separation of coarse materials with coarse material collection tank,
- an activation tank, consisting of an upstream denitrification and a nitrification tank for biological wastewater treatment,
- a membrane filtration system with immersed flat membrane filtration modules (type: siClaro® FM 622 from MMS AG) to separate the treated wastewater from the activated sludge and
- further treatment stages such as ozonation and activated carbon filter

In order to better understand the local situation of the wastewater treatment plants and the pilot plant, the following figure shows the locations of the GWSTP, the SINOWATER pilot plant and the NEPG together with their in-house wastewater treatment plant. The arrows with the solid lines represent water pipes. The arrow with the green line indicates the main inlet of the pilot plant, and the blue dotted line indicates the PA delivery (Fig. 4.10).

Figure 4.11 shows the test facility on the GWSTP site in summer and winter operation. The reservoir from which the municipal inflow was taken is shown in both pictures. The two storage tanks for the PA, which - like all inlet and outlet hoses of the container - were protected against frost on site with heating cables and foam due to the extreme weather conditions in winter. The pictures on the right show interior views of the plant. Several pictures of the individual operating phases and aggregates can be found in the appendix.

4.1.2.2.3 Project Progress and Operational Phases

The project is subject to different phases. In Germany, the trial period was essentially designed, constructed and transported to the project site on the basis of an evaluation of existing basic principles. After about two months by sea and a successful customs clearance, the pilot plant was delivered to the preselected treatment plant in Shenyang on 09.05.2017.

Fig. 4.10 Constellation of the Shenyang municipal wastewater treatment plant (GWSTP) with the pilot plant and the NEPG wastewater treatment plant

Fig. 4.11 SINOWATER experimental plant in summer (top), winter (bottom left) and interior views (right) (FiW)

On site, the piping for the PA inlet and further treatment stages such as the flocculation tank, the filtrate tank for ozonation etc. were further installed. After a frictionless clear water test, inoculation sludge was added to the activation. However, after a 2-month test operation phase, the pilot plant had to be moved to the other GWSTP treatment plant, as it turned out that the new treatment plant built almost 2 years ago could still not be put into operation due to the unclarified state of the sewerage system. The wastewater from the surrounding industrial area, which was delivered in batches as an alternative, was extremely highly contaminated (presumably untreated) and not suitable for commissioning (or sludge inoculation). During the test phase, a large amount of foaming activated sludge was observed from the deaeration pipe despite COD elimination of over 90% after membrane filtration.

The regular operation of the SINOWATER pilot plant extended from 08.2017 to 03.2018. The period can be divided into 3 major operating phases: Construction and commissioning / start-up phase, test phase for T1 with the municipal wastewater generated at the GWSTP treatment plant, and test phase for T2 with co-treatment of pharmaceutical wastewater. Among the last two major test phases, further individual test phases with different purposes are planned. Table 4.7 provides an overview of all test phases.

4.1.2.2.4 Sampling, Measurement Methods and Parameter Determination

The main sampling and sampling points and the parameters determined by them are listed in Table 4.8. To determine the wastewater parameters in the inflow and outflow of the test facility, a mixed sample was taken daily, consisting of three 600 ml samples at the same time. The inflow and outflow samples were taken from the reference treatment plant's receiving tank or from the respective sampling point at 9:00, 12:00 and 15:00 h and mixed in a collecting tank. For the laboratory analysis approx. 500 ml were then filled into a bottle and handed over to the laboratory staff. Furthermore, the sludge parameters were regularly checked by means of random samples from the aeration tank and filter chamber. With the exception of the sampling for the outlet to GAK-Filter all samples could be taken from the cleaning stages by ball valves.

The parameters to be determined for each test phase were selected according to the operating conditions. All analysis results were documented by sampling protocols, which are shown in the appendix.

The MBR test plant was controlled by a switch box with an integrated PLC touch panel. Since the plant was fed with different throughputs, in the test phase T2 with different mixing ratios of municipal and pharmaceutical wastewater, as well as with different additives, the operating parameters had to be constantly changed or adapted. The most frequently changed parameters on the touch panel are:

- Plant throughput
- Aeration time Nitrification (and denitrification)
- Flocculation system settings (including running time of FM and FHM pump, mixing time, total time)
- Volume throughput until the next ÜSS delivery

Determination of the Immediate Parameters

Immediate parameters are the parameters that are measured immediately after sampling. In the project, the following parameters were measured for each in- and outflow mixed sample:

- pH value [-]
- Conductivity [$\mu\text{S}/\text{cm}$]
- Oxygen content [mg/L]
- Temperature [$^{\circ}\text{C}$]

The measurements of the immediate parameters were carried out with the device "HQ40d" from the company "Hach" (portable 2-channel multimeter). Three different measuring probes were required for the pH value, conductivity and O₂ content. The temperature could be determined with the pH probe and the conductivity probe. Furthermore, odour, turbidity and visual colouration of the samples were observed and their changes documented. The on-site parameters give a first impression of the condition and treatability of the wastewater.

Due to the low temperatures during the project duration in winter, measurements with the device were no longer possible and the measuring device had to be moved

from the container to the laboratory about 400 m away after a short time. As a result, it was not possible to take oxygen and temperature measurements of the drains (before and after the activated carbon filter) and the inlets after a short time. The measurements of the pH-values and the conductivity could still be carried out in the laboratory of GWSTP.

Determination of the Sludge Parameters

The sludge parameters measured during the tests were:

- TS (Dry matter content) [g/l]
- SV30 (Sludge volume after 30 min) [ml/l]

The SV30 was determined in a 1 L standing cylinder daily for the sludge from the filter chamber and nitrification. Typically, the SV30 should be between 1,000 and 1,500 ml/L during operation. A description of the determination procedure is given in the appendix.

The dry matter content is tested by filtering the sample, then drying the filter residue and weighing it. The dry matter content was also determined during the project for the sludge from the filter chamber and the nitrification. It should be noted that the dry matter content of the nitrification is between 8 and 12 g/L and slightly higher in the filter chamber up to 16 g/L.

The addition of e.g. PAH increases the dry matter content. The SV30 is also affected by this. In order to be able to comply with the mentioned value ranges, the sludge discharge or the plant throughput must be changed or adapted. (MMS, no year).

The following parameters were determined for the pharmaceutical wastewater:

- TR (Dry residue) [%]
- oTR (organic Dry residue) [%]

The difference between the TS content and TR or oTR is that the sample is first filtered when determining the TS content. Thus only undissolved substances are dried. For the determination of the TR the whole sample is dried without previous filtration. To determine the oTR, the dish with the dried sample (after weighing for the TR determination) is heated to about 500 °C, so that all organic residual parts are burnt. The proportions can be calculated from the respective differences.

Determination of the Wastewater Parameters

Table 4.8 already lists the tested wastewater parameters (sum parameters). Daily sampling was carried out in order to check the cleaning performance of the MBR pilot plant and to control the inlet and outlet qualities. The local laboratory of SWSTP could be used during the whole project duration and on behalf of FiW the laboratory staff carried out most of the tests according to the standards of the Chinese Ministry of Environment.

Table 4.9 below lists the determination procedures used for the various parameters according to the respective Chinese standards.

4.1.2.3 Demonstration Results and Recommendations for Upgrading Actions in Shenyang

4.1.2.3.1 Presentation and Comparison of Results

The operation of the pilot plant with the mechanically pre-treated inflow wastewater of the reference wastewater treatment plant GWSTP, which serves the purpose of subproject T1, extended from 01.08.17 to 23.11.17. Furthermore, the two supplemented test series can also be assigned to T1 due to the lack of pharmaceutical wastewater during the T2 phase, namely the tests from 09.01.18 to 14.01.18 and from 19.02.18 to 23.02.18, respectively. The results of the first three series of tests of T1 (see Table 4.7) are presented and analysed in this chapter. For the analysis, calendar data of the sampling were assigned to numbers in the Numbers diagram. This is shown in Annex 4–8 in the Appendix.

Table 4.10 first lists the measured parameters in the inlet of the test plant during operation phase T1. With an average value of 7.9 and a standard deviation of 0.4,

Table 4.9 Determination procedure for wastewater parameters

Parameters	Determination method and standards	Determination limit
COD [mg/l]	Acidified sample is strongly heated with potassium dichromate. From the oxidized potassium, which is equivalent to the oxygen demand, dichromate the parameter. (GB11914-89, 1989)	16 mg/l till 700 mg/l
BOD ₅ [mg/l]	Sample saturated with oxygen is stored in a closed container under exclusion of light at 20°C for 5 days. The difference between the oxygen content measured before and after is used to calculate the parameter. (HJ 505-2009, 2009)	Undiluted: 2 mg/l till 6 mg/l Diluted: 6mg/l till 6000mg/l
NH ₄ -N [mg/l]	Spectrophotometry of a Neßler reagent to which a part of the sample has been added. Cuvettes and instruments from HACH Lange were used for the determination. (HJ 535-2009, 2009)	from 0,025mg/l depending on the used cuvette
TN [mg/l]	UV spectrophotometry of a cuvette from HACH Lange that has been mixed with part of the sample. Cuvettes and instruments from HACH Lange were used for the determination. (HJ 636-2012, 2012)	from 0,05 mg/l depending on the used cuvette
NO ₂ -N [mg/l]	Spectrophotometry of a cuvette from HACH Lange Cuvettes and instruments from HACH Lange were used for the determination. (Hachlange Schnelltest)	from 0,015 mg/l
NO ₃ -N [mg/l]	Spectrophotometry of a cuvette from HACH Lange Cuvettes and instruments from HACH Lange were used for the determination. (HACH Lange rapid test)	from 0,015 mg/l
TP [mg/l]	Spectrophotometry with ammonium molybdate as oxidizing agent for the decomposition of phosphorus compounds. (GB 11893-89, 1989)	from 0,01 mg/l depending on the used cuvette
SS [mg/l]	Filtering of the sample through filter paper with a pore size of 45 µm and subsequent drying of the filter paper at 103°C to 105°C until the weight is constant. (GB 11901-89, 1989)	-

Table 4.10 Parameters in the inlet of the test plant

	Parameters	n	Ø	Max	Min	s	Unit
Instant Parameters	Water temperature	78	20,9	33,4	9,1	4,4	[°C]
	pH value	82	7,9	8,7	7,3	0,4	[-]
	Conductivity	81	1468,8	1987,0	887,0	199,8	[µS/cm]
	Oxygen content	72	3,3	6,7	0,14	1,2	[mg/l]
Was te wa te	COD	89	191,4	371,0	102,0	52,5	[mg/l]
	BOD ₅	65	67,7	143,0	24,1	22,2	[mg/l]
	NH ₄ -N	89	29,6	57,3	14,0	6,8	[mg/l]
	TN	89	34,1	59,6	18,8	6,8	[mg/l]
Rati o	TP	55	3,6	12,0	2,0	1,6	[mg/l]
	SS	67	111,1	348,0	24,0	53,6	[mg/l]
	COD : BOD ₅	65	3,0:1	6,4:1	1,4:1	1,1	[-]
	BOD ₅ : TN	65	2,1:1	4,7:1	0,9:1	0,8	[-]

the pH value is in the optimum range between 7.5 and 8.5 for a biologically based wastewater treatment. The water temperature is also above the minimum temperature of 12 °C with an average value of 20.9 °C. As can be seen in the table, data sets of different sizes are available for the individual wastewater parameters, especially for BOD₅ and TP. The reasons for this were limited capacities, insufficient available materials and defective analysis equipment in the laboratory of the reference sewage treatment plant. Based on the analysis data, an average COD:BOD₅ of 3:1 was available in the influent, which is above the optimal ratio for a biodegradability of 2:1. Furthermore, the average COD₅:N ratio of 2.1:1 was below the minimum ratio of 2.5:1.

At the beginning of commissioning, the MBR pilot plant first had to be run in. For the time being, the cleaning performance was in the background. Rather, the aim of the start-up phase was to achieve and maintain the following basic requirements for a stable and reliable cleaning performance:

- Inoculation of the aeration tank with activated sludge from the reference treatment plant
- Concentration of the activated sludge to a dry substance value of at least 8 mg/l as well as a basic SV30 value between 1000 ml/l and 1500 ml/l in the aeration tank
- Slowly increase the total throughput to at least 400 l/h and simultaneously
- Prevent the diaphragm pressure from falling below –150 mbar

The MBR + C-Source test series is presented here as an example of the 4 test series with municipal wastewater.

MBR + CSource

In order to investigate whether the cleaning performance of the test plant against nutrient parameters could be improved compared to the normal MBR test series by increased degradability in the influent, glucose was added to the activation (deni

zone) as an external C-source in the form of solution by means of a peristaltic pump in the subsequent operating phase. Basic operating data and parameters are shown in Table 4.11. The measured inflow concentrations during the 22-day test phase resulted in a COD:BOD₅ ratio of 2.8 and a BOD₅:N ratio of 2.2, which is still outside the optimum condition. The aim of the addition is to raise the BOD₅:N ratio to about 4.5 to 5. The dosing quantity was based on the optimal requirement for a functioning denitrification on the basis of the worksheet DWA-A 131 and was calculated or adjusted with the average values from the previous concentrations of BOD₅ and TN in the feed. The BOD₅:N ratio is now an average of 5.5:1, so that sufficient readily degradable carbons should be available for denitrification processes.

However, due to the addition of glucose, sludge production increased, which meant that excess sludge had to be removed from the system more frequently. As a result, the sludge age in this operating phase fell to around 20 days. The high standard deviation of 6.5 days results from the adjustment of the discharge cycle for the excess sludge. Furthermore, the data from the filtration chamber show that the filtration properties deteriorated during this operating phase. The gross throughput initially had to be adjusted occasionally due to the transmembrane pressure being

Table 4.11 Operating conditions and operating parameters of the “MBR + C dosing” operating phase.

	Parameters	n	Ø	s	Unit
Inlet parameters	Net throughput	22	343,3	41,5	[l/h]
	Water temperature	14	15,9	2,6	[°C]
	pH	14	7,6	0,1	[-]
	COD : BOD ₅ (glucose free)	15	1,8:1 (2,8:1)	0,4 (0,9)	[-]
Aeration tanks	BOD ₅ : TN (glucose free)	15	5,5 (2,2)	1,0 (0,4)	[-]
	SV30	15	1195	95,8	[ml/l]
	TS	16	10,8	0,8	[g/l]
	Room load (glucose free)	15	0,63 (0,26)	0,06 (0,05)	[kgBSB ₅ /(m ³ *d)]
	Sludge load (glucose free)	15	0,09 (0,02)	0,01 (0,004)	[kgBSB ₅ /(kgTS*d)]
	Sludge Age	16	20,1	5,0	[d]
	Water temperature Nitrification	15	19,2	0,6	[°C]
	Oxygen content Nitrification	22	1,9	0,2	[mg/l]
	Retention time	22	2,8	0,3	[h]
	Reflux ratio	22	6,8	1,1	[-]
Filtration chamber	Gross throughput	22	429,2	51,9	[l/h]
	Transmembrane pressure	22	-113,6	22,0	[mbar]
	Membrane flow	22	8,6	1,0	[l/(m ² *h)]
	Permeability	22	77,1	10,7	[l/(m ² *h*Bar)]
	Retention time	22	3,5	0,4	[h]

undershot and therefore averaged only -113.59 mbar. As a result, the membrane flow also dropped to $8.58 \text{ l}/(\text{m}^2 \cdot \text{h})$. As a result of the lower membrane flow and the higher average transmembrane pressure, the permeability of $77.05 \text{ l}/(\text{m}^2 \cdot \text{h} \cdot \text{bar})$ was lower than in the “MBR” operating phase. The reduced membrane performance is due to a stronger top layer formation caused by the higher sludge production, which is triggered by the addition of glucose. As a result of the reduced membrane performance, the net throughput decreased, which slightly increased the return ratio during the operating phase. The average residence time in the aeration tank was about 2.8 h and in the filter chamber about 3.5 h. The sludge parameters and the oxygen content fluctuated within the assumed values.

The calculated increase in COD concentration is shown in Fig. 4.12. As in the operating phase “MBR”, there were strong fluctuations in the COD concentration in the feed, which ranged between 110 and 370 mg/l. In order to accustom the microorganisms to the carbon load by glucose, only half of the calculated amount of glucose was dosed by day 94. From day 95 onwards, the COD concentration was increased by 136 mg/l on average. The outflow concentration reached a maximum of 40 mg/l and averaged 25 mg/l. The effluent concentration of 50 mg/l of SK IA was maintained on each measured day. An average COD elimination rate of 92% was achieved, which ranged between 86 and 97% over the period. Not shown are effluent concentrations of BOD₅ which do not exceed a concentration of 1.6 mg/l and thus elimination rates between 98% and approximately 100% were achieved.

Figure 4.13 shows the measured nitrogen concentrations during glucose dosing. The $\text{NH}_4\text{-N}$ concentration was completely eliminated so that no concentration could be detected in the vicinity. According to the measured values, a change in the TN concentration in the effluent and the TN elimination rate due to the provision of glucose only occurred slowly from day 95 onwards. The inflow and outflow values measured from then on on 13 days resulted in an average elimination rate of 47%. On day 103 this reached its highest value of 63% and led to the lowest effluent concentration of 10 mg/l. Due to the reduction of $\text{NO}_3\text{-N}$ to elemental nitrogen,

Fig. 4.12 COD concentrations in the inflow and effluent of the pilot plant and elimination rates during the addition of glucose

Fig. 4.13 Nitrogen concentrations in the inflow and effluent of the pilot plant and elimination rates during the addition of glucose

which escapes as a gas, an average effluent concentration of 15.37 mg/l occurred. The future required effluent concentration of SK IA (15 mg/l) was met on 6 days.

An improvement in phosphorus elimination through the addition of an external carbon source was also noticeable from day 95. The concentration in the effluent decreased to a value of 0.5 mg/l on day 103, while at the same time the elimination rate reached the maximum value of 82%. The highest effluent value was reached on day 111 with a concentration of 1.4 mg/l. Here, however, the highest concentration was also measured in the inflow of about 4.0 mg/l. Due to the average elimination rate of 71% from day 95 on, the future required effluent concentration of 1.0 mg/l of SK IA was met with an average effluent concentration of 0.90 mg/l. More precisely, the standard was met on 8 of the 12 days measured. The reason for the higher elimination rate is the additional supply of carbon. As already explained, the presence of easily degradable carbon is a basic prerequisite for the incorporation of phosphorus into the biomass-water (Fig. 4.14).

One of the changes in the cleaning performance of suspended solids has not been shown during this operating phase. The average elimination rate of suspended substances was approximately 100%. The following table summarizes the average concentrations and elimination rates of all parameters (Table 4.12).

Comparison of Results

The test results obtained from all test series during the project phase T1 can be evaluated as follows. After successful commissioning, the sludge solid content (dry matter content) in the aeration tank and in the filter chamber was in the range between 10 and 14 g/l, which corresponds to the usual operating values of MBR. The membrane transfer pressure and membrane flows could also be maintained in the desired operating ranges. The throughput of the plant depends on the membrane performance. From the running-in phase to the last operating phase it can be seen that initially the concentration of the activated sludge led to a reduction of the flow or the permeability of the membrane despite the strong and regular air flushing in the filter chamber.

Fig. 4.14 Total phosphorus (TP) concentrations in the inflow and effluent of the pilot plant and elimination rates during the addition of glucose

Table 4.12 Compilation of inflow and effluent concentrations and elimination rates during glucose dosing

Parameters		Inflow [mg/l]		Outflow [mg/l]		Elimination rate [%]	
Description	n	Ø	s	Ø	s	Ø	s
COD	15	315	68	25,0	9,0	92%	3%
BOD ₅	4	153	18	1,0	0,5	99%	1%
NH ₄ -N	15	25	4,6	0,1	0,2	99%	1%
TN	13	29	3,6	15,4	3,0	46%	8%
TP	13	3,2	0,5	0,9	0,3	71%	8%
SS	14	97	31,0	0,3	0,3	100%	1%

The membrane flow decreased from just under 12 l/(m² * h) in the MBR phase to 6 to 8 l/(m² * h) in the supplementary phases while maintaining the optimum transmembrane pressure range with the aim of achieving the best possible purification performance in the research project. In practice, a constant throughput is also possible, however, taking into account that the membrane pressure must not exceed the maximum upper limit (in the case of the project – 300 mbar) and that the cleaning performance can be impaired by increasing the pressure.

In addition, the performance of the membrane was impaired by the addition of glucose, flocculant and PAH, as the increased sludge production resulted in a stronger top layer. However, membrane filtration allows the adjustment of higher TS contents, resulting in a higher sludge load and a reduction of the reaction volume.

A comparison of the average effluent concentrations and elimination rates of the operating phases assigned to T1 with the literature values of the MBR plants in practice with simulated precipitation is shown in Table 4.13. The average COD effluent concentrations of the MBR pilot plant correspond to the literature values. Deviations between the test series can be found, but this is due to a high and fluctuating proportion of industrial wastewater or inert COD in the inflow. The effluent concentrations of BOD₅ are also very low. Easily degradable organic carbon was almost completely

Table 4.13 Comparison of the average effluent concentrations (a, mg/l) and elimination rates (e) of the pilot plant with literature values of MBR plants with simultaneous precipitation (based on DWA [18] Dohmann et al. [2] Pinnekamp et al. [3])

	MBR			MBR + C- Source			MBR + C+ FM			MBR + C + PAK			Literature value MBR plant with simultaneous precipitation
	n	a	e	n	a	e	n	a	e	n	a	e	
COD	22	19,0	90%	15	25,0	92%	5	28,0	86%	5	19,2	88%	< 30
BOD₅	11	1,2	98%	4	1,0	99%	-	-	-	-	-	-	<3,0
NH₄-N	22	0,1	99%	15	0,1	99%	-	-	-	-	-	-	<2,4
TN	22	28,0	16%	13	15,4	46%	5	10,2	68%	5	13,4	53%	< 13
TP	19	1,4	58%	13	0,9	71%	5	0,15	95%	5	0,11	96%	< 0,3
SS	22	1,6	99%	14	0	100%	-	-	-	-	-	-	0
TS	22	12,1	-	16	10,8	-	5	16,7	-	5	16,8	-	8 - 20

eliminated, which is why a very low concentration in the effluent was detected. This results in a good cleaning performance of the pilot plant of carbon compounds in the wastewater. The addition of flocculants and PAHs could not massively improve the COD effluent values. The COD concentration could be further reduced by a downstream activated carbon filter. However, this measure is not very interesting for upgrading municipal wastewater treatment plants because of the already very good effluent values in the filtrate of the MBR (far below the future limit value of 50 mg/l).

With regard to the effluent concentrations of nitrogen compounds, the literature values of the EN of MBR plants were not complied with in test series of the “MBR” without further measures. Almost no NH₄-N was detected in the effluent, which can be justified by the complete oxidation to NO₃-N. In this case, the converted NO₃-N was not reduced to elemental nitrogen, so that the effluent concentration of 28 mg/l was more than twice the expected concentration of less than 13 mg/l. Responsible for the incomplete denitrification may be the oxygen carry-over from the continuously aerated filter chamber. The continuous aeration, which enabled the cross-flow operation of the membrane filtration, could cause an undesired oxygen input into the wastewater-activated sludge mixture, which flowed via the overflow back into the upstream denitrification tank. As a result, the setting of an anoxic environment could be impaired, which could lead to a disturbance of the denitrification processes. Another cause is the bad C-N ratio in the raw sewage, which has already stoichiometrically strongly limited the maximum degree of denitrification. As a result of the addition of a C source, the TN effluent concentration is significantly reduced. Nevertheless, with improved BOD₅:N ratios the literature value or the limit value 15 mg/l of SK IA was not continuously reached. It should be noted that the term TN or Nges in the German wastewater Ordinance only covers the inorganic nitrogen fractions. The wastewater produced contains a large proportion of industrial wastewater in which hardly degradable organic nitrogen compounds are present. For this reason, the effluent values of the “MBR + C-Source” operating phase are already comparable with the values in practice. However, the period of 24 days for the operation phase “MBR + C-Source” can also be the reason for an incomplete formation of the anoxic biocoenosis. Due to the limited time frame of the project, the operating phase

could not be extended. Although the data density and the reliability of the results are limited, the two supplemented test series during the project phase T2 showed a further improved denitrification performance with lower effluent values, which could confirm the positive effect of glucose addition and its reasonable dosage.

Furthermore, the TP effluent concentrations of the test plant showed relatively worse values than the literature value during the operating phase “MBR”. However, this value refers to MBR plants whose TP elimination rates have been improved by simultaneous precipitation. The biological phosphorus elimination was improved by the addition of C-source, whereby the effluent concentration dropped from an average of 1.4 mg/l to 0.9 mg/l and was already below the limit value of 1.0 mg/l. The achieved average TP elimination rates of 58% without C-source and 71% with C-source show that the pilot plant demonstrates biological phosphorus elimination. The addition of a chemical phosphorus elimination in the supplementary test series “MBR + C + FM” caused the effluent concentration to drop rapidly to 0.15 mg/l, which was fully in line with the literature values. Due to the limited time period, the simultaneous precipitation could only be investigated for a few days.

The analysis results of the SS concentrations confirm the desired values. Although concentrations were found in the analysis results in the effluent, these are due to measurement errors or unclean sampling. The complete retention of solids as well as of bacteria and viruses is a clear advantage for the use of the membrane activated sludge process.

For the wastewater produced in Shenyang, the addition of PAHs could not provide a significant cleaning performance. Due to fluctuating elimination rates and limited data capacity, no reliable assessment of the cleaning performance of powdered activated carbon could be made. The dry matter content increases with the addition of FM and/or PAH, but according to literature values it is still within the controllable range (<20 g/l). All in all, the pilot plant delivers an excellent cleaning performance when treating the rather industrial “municipal wastewater”.

4.1.2.3.2 Comparison of the Treatment Performance of the Pilot Plant with the Reference Treatment Plant “GWSTP”

In order to be able to evaluate the treatment performance in view of the nature of the wastewater, a comparison between the effluent concentrations of the reference treatment plant “GWSTP” and the pilot plant will be made, including the target effluent concentration, for classification in the SK IA. In this respect, Fig. 4.15 shows a comparison of the treatment performance of two representative test series of the test plant and of the large sewage treatment plant during the test period of project phase T1. First of all, it is noticeable that the test plant showed considerably better effluent concentrations than the reference treatment plant. It should be noted that the average effluent concentrations of the reference treatment plant are much higher, as they were analysed daily by the laboratory.

Apart from the number of values measured, there were also small differences between the sampling from the reference sewage treatment plant and the sampling from the experimental plant (Chapter 2.2.4). Due to the 24-h mixed sampling in the inflow and outflow of the reference treatment plant, the analysis results represent

Fig. 4.15 Comparison of the cleaning performance of the reference wastewater treatment plant "GWSTP" with the cleaning performance of the test plant in the operating phases "MBR" and "MBR + C-Source"

the average wastewater quality of the whole day, whereas the three-time sampling in the inflow and outflow of the test plant is only representative for the period from 9 a.m. to 3 p.m. During this period, more polluted wastewater was discharged due to the working hours of the industrial plants. Since the effluent values of the test plant correspond to the literature values and the cleaning performance of the membrane stage is relatively stable, these values can be used for a qualitative comparison with the effluent values of the reference treatment plant.

The COD and BOD and NH₄-N effluent concentration of the pilot plant is on average lower than in the reference treatment plant in almost every operating phase. This is due to the fact that the large sewage treatment plant did not have to comply with standard class IA before 2018. As already mentioned, the former plant design and faulty technical management are reasons for the high effluent concentration. In 2005, the large sewage treatment plant was designed with the main tasks of eliminating carbon and ammonium nitrogen and thus to comply with the effluent concentrations of standard class II. In order to be able to compare the load conditions of the two plants better, the following Table 4.14 shows the average room and sludge load of the two plants during the project phase T1. As "GWSTP" has additional carrier materials in the aeration tank operated with the HYBAS process, it is difficult to determine the exact sludge load. It is assumed that the use of free-floating carrier materials causes about 10% more biomass in the hybrid activated sludge zone.

Table 4.14 Comparison of the room and sludge load of the reference wastewater treatment plant “GWSTP” and the pilot plant in the operating phases “MBR” and “MBR + C-Source”

			Room load [kgBSB ₅ /(m ³ *d)]	Sludge load [kgBSB ₅ /(kgTS*d)]
MBR			0,37	0,03
MBR + C-Source			0,63	0,09
Water	treatment	plant	0,35	0,12 (0,14*)
„GWSTP“				

*: without consideration of carrier materials

Without the addition of an external C-source, the low room load of the test plant during the normal operation phase “MBR” is very close to that of the wastewater treatment plant, which reflects a good comparability of the two plants. It is noticeable that the low sludge load of the test plant of 0.03 according to DIN EN 12,556–6 rather points towards sludge stabilisation due to the high dry matter content and the guaranteed aeration, whereas the sewage treatment plant with 0.12 is only adjusted to the purification target nitrification, which can explain its limited purification performance in terms of N elimination. The average high TN effluent concentrations of the wastewater treatment plant and the operating phase “MBR” are initially due to the poor BOD₅:N ratio in the inflow. The difference between the two effluent concentrations can be assumed to be due to the additional coarse material cell in the test plant, which has removed some of the easily degradable carbon required, in addition to the reasons already clarified (oxygen carry-over). Furthermore, inadequate aeration of the sewage treatment plant may have led to anoxic conditions in the basin, which favoured certain formation of denitrification processes. With the addition of C-source, the sludge load of the pilot plant could be well adjusted to the target range of N-elimination and lower effluent values could be achieved.

The experimental plant did not show a significantly better performance in P-elimination without further measures (C-dosage or simultaneous precipitation). As expected, the SS concentration in the effluent of the treatment plant is significantly higher than the effluent concentration of the test plant. In summary, the test results show that the treatment performance of the test plant is better than that of the reference treatment plant without consideration of specific investment and energy consumption and leads to much lower concentrations of the wastewater parameters in the effluent. This treatment performance can be improved, especially with regard to nitrogen and phosphorus compounds, by adding a C-source and flocculants, since the nature of the wastewater to be treated alone does not allow for a better biological treatment.

4.1.2.3.3 Recommendations for Upgrading the Old Municipal Wastewater Treatment Plants in Shenyang

In principle, the investigations show that the pilot plant has a better purification performance than the reference sewage treatment plant in Shenyang. In view of the poor elimination rates of BOD₅ and NH₄-N, however, this is not due to the technology used, but to poor management of the reference treatment plant. This leads to the fact

that due to insufficient aeration and circulation of the aeration tanks, the optimal conditions for the biological carbon degradation and a functioning nitrification are not created. Therefore, the requirements for the technical operation should be adapted so that the purification performance of the process used can be improved.

On the other hand, some large municipal wastewater treatment plants in Shenyang do not aim for extensive nutrient elimination (cf. Chapter 2.3.2) due to the less stringent environmental requirements (required emission standard) in the year of construction, which is why the “GWSTP” lacks a separate denitrification zone and direct comparability with the pilot plant is limited. As a result of the tightening of the emission standard in the 13th five-year plan (from II or IB to IA) by the environmental authority, upgrading measures are mandatory at the relevant wastewater treatment plants in Shenyang from 2018. The GWSTP is primarily the conversion of the existing old biological stage into AAO basins, which are operated in hybrid mode with floating carrier materials and should provide a better cleaning performance with respect to nitrogen and phosphorus..

Furthermore, the C:N ratio in the inlet should be adjusted to allow denitrification processes to take place. The change in the C:N ratio can be achieved by reducing the amount of extraneous water and rainwater in the inflow, which is of great importance for Sponge City and for the effective purification performance of the wastewater treatment plants in Shenyang. This will lead to higher concentrations of wastewater parameters in the influent. The question arises whether the sewerage system should be regularly checked for leaks and damage and repaired if necessary to avoid dilution of the wastewater by extraneous water.

The additional discharge of industrial wastewater also results in a high load of easily degradable carbon. Furthermore, the dosing of an external carbon source can contribute to an improvement. For the conversion there is the possibility to control the substrate dosage into the aeration tank by means of a nitrate measurement in order to adjust the optimal C:N. The proportion of biologically non-eliminable organic residual N in the influent could be determined, for example, by the results of the test plant (maximum achievable TN effluent values and elimination rate under C overdosage or empirical values).

The biggest challenge for the GWSTP treatment plant are the industrial waste waters to be treated. This applies all the more, because in the future still further industrial enterprises are to be attached to the purification plant and clear production increases of the enterprises with accordingly increased wastewater quantities are expected. For this reason, a complete indirect discharge register must be drawn up, which should include all important and up-to-date information on the plants and their discharge status and is currently only available in small quantities. Due to the fact that many sewage treatment plants in Shenyang have only very limited access to it, the local environmental authorities responsible must exert influence here. The connection situation of the sewerage system must be examined more closely in order to be able to make more precise statements about the discharged industrial wastewater streams. On the other hand, online monitoring of the pre-treatment plant processes is urgently required, at least for the main companies. In order to be able to detect possible faults in the downstream sewage treatment plant at an early stage and to

initiate appropriate measures such as commissioning the emergency basin or dosing powdered activated carbon, the online data must be transmitted directly to the sewage treatment plant.

From the point of view of cleaning technology, a changeover to the membrane bioreactor process would only make sense in the short term if the cleaning performance of the Shenyang treatment plant in question is not sufficiently improved despite optimised technical management, conversion measures and wastewater conditions. Due to the usually low inflow concentrations, it was assumed in the conceptual planning that the use of MBR for the GWSTP treatment plant is not necessarily immediately sensible.

According to the already published annual plans or the current environmental policy of the Chinese central government, even stricter discharge standards will be required in the future, so that the upgrading of the old sewage treatment plants can take place. The definition of the discharge standard depends strongly on the water to be discharged. If sensitive waters or water resource protection areas are involved, higher standards must be achieved up to surface water quality. For this reason, the state discharge standard IA is tightened to varying degrees in many priority regions such as Beijing and the Taihu catchment area. In Shenyang and the Liaohe catchment area, this trend is also expected to continue in the near future. Figure 4.16: Comparison of the maximum achievable effluent quality of the pilot plant with the standard of the Chinese emission and surface water qualities shows the maximum achievable effluent quality (average values of test series) of the pilot plant and the standards of the Chinese emission and surface water qualities. With the exception of TN, most of the achievable effluent values comply with the Chinese standard of surface water quality class III, which is suitable for use as fishing water or for drinking water treatment. In this sense, the use of MBR in Shenyang or the catchment area of Liaohe can be advocated in the long term.

In view of higher operating costs due to higher energy consumption, it must be weighed up whether the advantages of MBR contribute to a meaningful improvement in cleaning performance in each individual case. From the results of the trials carried out in the project, the Sinowater concept offers the following advantages for upgrading the wastewater treatment plants in Shenyang:

- The choice of a sustainable German system with low-maintenance flat membranes (as in the pilot plant) guarantees a minimum operating time of 10 years for the first time.
- The process option tested in project phase T1 results in a higher biomass concentration (10–12 g/l), a desirable higher sludge age and thus a considerable saving of reactor volume and space (4 times as much as GWSTP with a TS content of 2.5 g/l), which can be of great importance for the rapidly developing Chinese metropolises like Shenyang.
- The flow paths of the wastewater in the sewage treatment plant area are thus simplified.
- A germ-free and solid-free effluent is created which enables, for example, a reuse of the wastewater.

Fig. 4.16 Comparison of the maximum achievable effluent quality of the pilot plant with the standard of Chinese emission and surface water quality

- Secondary settling tanks can also be dispensed with. Necessary further treatments, which have to be requested by the environmental authorities at short notice or in the future, such as odour removal by means of a soil filter, can be carried out in existing saved plant components.
- Simultaneous dosing of external carbon sources into the MBR can be easily controlled. In case of disturbances caused by industrial wastewater, the dosing of powdered activated carbon or flocculant into the MBR is recommended.

In the case of upgrading by the MBR process, Fig. 4.17 shows 3 implementation variants based on the recommendations of the DWA, for example at the reference wastewater treatment plant GWSTP, with the concept of not building the nitrification stage separately but integrating it into the membrane stage. In the first option, the secondary clarifier is to be converted to an upstream denitrification stage and the aeration tank is to be used as a membrane stage, whereas in the second option the circuit is to be reversed. The tank volumes saved in this way can be used for another purpose. In the third option, the secondary settling tank can be completely converted for further treatment to improve the cleaning performance. Depending on the required dimensions, the conversion measure should be carried out taking into account the existing tank volumes. For example, a ratio of 1:1 is recommended for the volume ratio of denitrification and nitrification tanks in order to reduce oxygen carry-over through the return flow. In general, calming zones before the sludge recirculation should be provided in practice to avoid oxygen carry-over into the denitrification

Fig. 4.17 Proposals for upgrading the reference wastewater treatment plant GWSTP to the MBR process

area or to optimise oxygen utilisation in the nitrification area. In addition, in the case of the spatially separated filtration area, it is also advisable to return the return sludge to the nitrification zone. In this way, both sludge circuits can be set separately from each other Pinnekamp and Friedrich [19]. In order to maintain the performance of the membrane modules in the long term, the mechanical pre-treatment would have to be supplemented with a grease trap which can be integrated into the aerated grit trap.

4.1.2.4 New Approaches to the Co-treatment of Pharmaceutical Wastewater in the Municipal Treatment Plant

In this chapter the results of the individual test series from the large project phase T2 (co-treatment of pharmaceutical wastewater) are presented first. In order to ensure the comparability of the different test series, not all parameters were examined due to the large amount of data. Due to the fact that parameters such as $\text{NH}_4\text{-N}$, SS and BOD₅ could be almost completely eliminated in all test series, the inflow and outflow values of COD are therefore preferably compared and the elimination rate calculated for each test series. For most of the test series, however, additional measured data

of nutrient parameters are given, which allows statements to be made about the effectiveness of the respective procedure.

The project phase began on 24.11.2017, the date on which the pharmaceutical wastewater was finally available after several local clarifications and coordination. The PA proportion in the total inflow is always given as a mass percentage. According to measurements of the local laboratory, the density of the two wastewater substreams corresponds. Like the presentation of project phase T1, each measured day is assigned a number between 1 and 87 (see appendix). Since the series of measurements did not all take place in a coherent manner, the horizontal axes of some diagrams will not show any coherent numerical sequences.

Near the SWSTP, a new treatment plant will be in running-in operation from 10.2018. This treatment plant will also be fed with the mixed inlet of municipal and pharmaceutical wastewater. The expected PA content will be 28%, so that during the project a PA content of 28% was aimed for in order to test the conditions to which the new sewage plant in Shenyang will also be exposed. On this basis, a recommendation for further purification processes will be made, which could be considered for this and other wastewater treatment plants in the region. In order to test the treatment limit of the pilot plant, the PA content was further increased to 100% at the end of the project. The cleaning performance of the pilot plant will be evaluated for the mixed PA and municipal feed.

4.1.2.4.1 Description Of the Inflow Situation of The Pilot Plant

The total inflow consists of the partial flow municipal wastewater and the partial flow Pharma wastewater. The municipal wastewater, which was treated in the test plant, was taken unchanged as before from the inlet to the biological treatment stage of the “GWSTP” above the submersible pump. Apart from the COD values, most of the inflow values of this partial stream could be assumed to be relatively constant during the entire project phase, with only a few larger deviations. The following diagram shows the concentrations of COD (mean value 176.10 mg/l), BOD5 (mean value 68.35 mg/l), TN (mean value 30.66 mg/l), and TP (mean value 3.02 mg/l) as representative values. The proportion of $\text{NH}_4\text{-N}$ in TN is on average 80%.

As explained in Chapter 5.1, the pharmaceutical wastewater (PA), which was also treated in the pilot plant, has already undergone operational pretreatment, was taken from the effluent of the NEPG treatment plant and delivered to the pilot plant in batches as required. The concentrations of the main parameters in the pharmaceutical wastewater are also shown in Fig. 4.18. It is noticeable that the concentrations of the constituents in the PA vary greatly from batch to batch compared to the municipal partial flow, which means that the load on the biology in the test plant also varied greatly. The commissioning of the membrane stage from day 52 in the NEPG wastewater treatment plant improved the effluent values of the treatment plant considerably, especially for the COD and BOD5.

Figure 4.19 shows the proportion of PA and the COD values representing the mixed feed (COD from the two partial streams and from the mixed feed). It can be seen that the proportion of PA mainly had an influence on the COD feed values of the mixed feed when the COD feed concentrations of PA (before day 52 or commissioning of

Fig. 4.18 Inflow values of the partial flow municipal wastewater (top) and the partial flow pharmaceutical wastewater delivered in batches (bottom) over the measured period for T2

Fig. 4.19 Influence of the PA content on the mixed feed (COD)

the mixed feed) were very high. However, no direct conclusions can be drawn from the level of the PA content itself. The downstream municipal wastewater treatment plant of Shenyang is also confronted with this circumstance, as the discharge values of the operational wastewater treatment plant of the pharmaceutical company (and presumably other companies) are subject to strong fluctuations. It can also be seen that the COD:BOD5 as well as the BOD5:N ratio in the partial streams - and thus also in the mixed feed - is not at all optimal. Especially in PA, the BOD5 values are mostly below the TN concentrations due to the pre-treatment and do not exceed 30 mg/l from day 46. In order to set the desired ratio, the dosing of C-source into the revitalization was continued during the project phase T2. The glucose solution (175 g/L) had a COD value of about 187,000 mg/l.

The individual batch duration (shown in Fig. 4.18) changes during the entire project period, especially from the beginning to day 22 due to the adjustment of the coating ratio until the desired proportion of PA is reached, and from day 81 due to the further increase of the PA proportion up to 100%. A slight fluctuation of the PA content during the stable feeding phase between day 22 and day 81 can be attributed to the occasional operational disturbances and sludge discharge. The working conditions during the entire project period (measuring days 1 to 87), which influence the plant performance, are shown in the table below, together with the standard deviation. Operating conditions and parameters for individual operating phases/series of tests can be found in the appendix (Table 4.15).

4.1.2.4.2 Presentation of the Results of Important Operating Phases

According to Table 4.5 different test series have been carried out. The results of the MBR, MBR + GAK, MBR + ozone + GAK and MBR + PAK test series are presented below as examples.

MBR

In this chapter, only the days are examined on which the pilot plant was tested without the application of further purification stages. A total of 34 measuring days can be assigned to this phase. As already mentioned, two membrane modules of the type FM 622 of the company siClaro® are installed in the filter chamber, so that the membrane surface, the flow rates as well as the purge air requirement of a single module can be doubled. The limit data of a module and the plant are shown in the appendix. The flow and the membrane pressure must not exceed the upper limit ($22 \text{ l}/(\text{m}^2 \cdot \text{h})$ or -300 mbar), otherwise the membranes may be damaged. A first automatic error message was given at -150 mbar . According to the manufacturer's specifications, the membrane pressure should be below -100 mbar for optimum cleaning performance, as explained, which was also to be aimed for during the operating phase. The membrane pressure depends on the sludge properties, the wastewater constituents, the throughput of the filtrate pump (in the course of which the membrane flow and permeability) and the flushing air volume flow. Especially by changing the flow rate as well as the dry matter content, the membrane pressure could be significantly influenced, as shown in the diagram below (Fig. 4.20, $n = 34$). Each measured value for the diaphragm pressure is a representative value of the respective measuring day. In

Table 4.15 Operating conditions of the test facility for project phase T2

	Parameters	n	Ø	s	Unit
Inlet parameters	Net throughput	87	292,3	53,2	[l/h]
	pH	85	7,69	0,8	[-]
	COD : BOD ₅ (without glucose)	85	2,3:1 (4,8:1)	2,0 (3,0)	[-]
	BOD ₅ : TN (without glucose)	85	4,1 (1,1)	1,4 (1,2)	[-]
Aeration tanks	SV30	64	1053	145	[ml/l]
	TS	64	12,8	1,9	[g/l]
	Room load	BSB	76	0,56	[kg/(m ³ *d)]
		CSB	87	1,28	
	Sludge load	BSB	64	0,045	[kg/(kgTS*d)]
		CSB	64	0,098	
	Sludge age	87	22,9	5,1	[d]
	Water temperature Nitrification	60	19,0	1,0	[°C]
	Oxygen content Nitrification	87	2,0	0,5	[mg/l]
	Retention time	87	3,2	0,5	[h]
Filtration chamber	Reflux ratio	87	6,1	2,1	[-]
	Gross throughput	87	365,4	66,1	[l/h]
	Transmembrane pressure	87	-96,6	22,0	[mbar]
	Diaphragm flow	87	7,5	1,3	[l/(m ² *h)]
	Permeability	87	84,7	25,2	[l/(m ² *h*Bar)]
	Retention time	87	4,1	0,6	[h]

addition, the membrane pressure is influenced by the addition or residual amount of various substances such as PAH or FM remaining in the system (from day 54, increased DM values as a result of the residual effect of FM or PAH dosing). It can be seen that the diaphragm pressure decreases or increases with a slight time delay in response to a change in flow. The correlation for the displayed curves is $R = 0.59$. After shifting the measuring days by two days, the correlation is $R = 0.65$.

The working conditions prevailing during the test phase are comparable with those shown in Fig. 4.21. Figure 4.21 shows the COD inflow and outflow values of the test plant as a function of the PA content ($n = 34$). The respective COD contents in the mixed feed can also be seen. As already mentioned, glucose was added to the mixed feed in order to support the decomposition of nitrogen. As a reaction to the high TN feed values of the PA (>82 mg/L) of the test phase “Further increase of the PA proportion”, the glucose dosage was greatly increased from day 82.

It can be seen that the limit value of 50 mg/l can almost always be adhered to in the beginning. In the rear part of the diagram, however, it is exceeded, which is mainly due to the PA content of the mixed feed, which in the end has been increased to 100% over a few days. It is noticeable that the effluent concentrations, especially from day 54 onwards, are for the most part higher than the PA concentrations, and for the last four days only slightly lower than the PA concentrations, which indicates the extremely

Fig. 4.20 Relationship between membrane flow, dry substance content and membrane pressure

Fig. 4.21 Inflow and effluent concentrations as a function of PA content during the operating phase MBR

poor degradability of the COD in the PA (especially in the PA already subjected to the operational membrane stage, in contrast to the COD content of glucose). In order to indicate this phenomenon, Fig. 4.22 shows the correlation between the COD elimination rate (related to the mixed feed without considering an additional C source) and the PA content in the mixed feed. On the other hand, it can be interpreted from the slidegram that in the industrial “municipal wastewater”, a part of the COD can also neither be eliminated by biological stage nor by ultrafiltration. In order to be able to effect a degradation of the inert COD, further purification processes were tested (see following chapters).

During the operating phase, the future TN limit of 15 mg/l can only be complied with on three days with the addition of additional C-source. Despite the fluctuation in the mixed feed, a stable and orderly elimination line can be seen up to day 61. The poor effluent values on the rear days confirm that a large part of the nitrogen present

Fig. 4.22 Membrane flow & correlation between PA content and COD elimination rate of the pilot plant related to the mixed feed without glucose dosing

in the PA, as with COD, is also inert, i.e. biologically non-degradable or hardly degradable. This part is rather due to the refractory organic nitrogen compounds in pharmaceutical production (Fig. 4.23).

For the parameters NH₄-N, BSB₅ and SS the plant delivers fully satisfactory results, and due to the somewhat low concentrations in the PA feed, the P elimination with an average effluent value of 0.54 mg/l has been much improved compared to project phase T1. The average elimination rates as well as inlet and outlet concentrations of all parameters are shown in the following table. The COD elimination rate here refers to the mixed feed with C-dosage. For the calculation of the data, representative time periods were selected in which the PA content does not exceed 28% and is not influenced by previous test series (e.g. between day 26 and 69).

Fig. 4.23 Inflow and effluent concentrations of TN as a function of PA content during the operating phase MBR

Fig. 4.24 Change in COD concentrations due to downstream GAK filter

MBR + GAK

The Granulated Activated Carbon Filter (GAK) was also put into permanent operation during project phase T2. In order to be able to assess the effectiveness of the GAK in direct comparison to the plant without GAK, Fig. 4.24 shows the COD discharge values for the same measuring days for the above described operating phase “MBR” and for “MBR + GAK”. On a total of 23 of the 34 days of the “MBR” operating phase, the process could be analysed according to GAK. This clearly shows that the GAK filter further increases the cleaning performance. Only on one day the COD discharge of the filter is above that of the test plant. This value can be justified by measurement inaccuracy, as the values only differ from one another by 4 mg/L. It can also be seen that even the GAK filter cannot significantly reduce the inert COD content any further, especially if the PA content is increased to 100%. The average COD elimination rate between the MBR filtrate and the GAK drain for the measuring days is 18.26% (without measuring day 15).

The average COD concentration of the mixed feed, the average COD effluent concentration of the MBR (filtrate) and MBR + GAK and the average COD elimination rate in relation to the mixed feed with glucose are shown in Table 4.18 below (COD in relation to the mixed feed with C source). In order to achieve uniformity of presentation, the operating phase “Increase in proportion of the PA” is also not included in the statistics here. It can be seen that the elimination rate can be increased by approx. 2% by using the GAK. In relation to the mixed feed without glucose, it is even almost 5% (Table 4.17).

Table 4.18 shows the elimination rates as well as inlet and outlet concentrations for the measured parameters. For TP and TN no significant improvement could be found by using GAK and due to the workload of the laboratory not many measured values could be collected, which limits the data reliability.

Preozoning + MBR + GAK

During pre-ozoning, the PA partial water stream was ozonated before it merged with the municipal wastewater partial stream. The exact dosing point is shown in Fig. 4.9.

Fig. 4.25 Inflow and effluent concentrations of the operating phase preozoning + MBR + GAK

The original aim of the pre-ozonation of the PA partial flow is that a favourable substrate supply (improved BOD:COD or BOD:N ratio in the inflow) for the microorganisms in the aeration tank can be achieved by splitting up the hardly degradable molecules and compounds in the PA. The ozone was added to the PA partial water stream via a diffuser while it was pumped from the flocculation tank through a pipe in the direction of the confluence of the two partial water streams. In the first series of tests with air supply, the dosing quantity of ozone was fixed at approx. 12 mg per litre of feed PA on the basis of preliminary tests carried out in the laboratory, and in the second series of tests with oxygen supply it was increased to approx. 30 mg/l. The COD inlet and outlet values of the plant are shown in Fig. 4.25. In addition, samples were taken on some days not only from the filtrate but also from the GAK filter, and these values are also shown.

From the 7-day trials it can be seen that the limit value of 50 mg/L can always be complied with. It is noticeable that the effluent values do not look particularly better in comparison to operating phases without ozonation and that the cleaning performance cannot be increased with higher ozone dosage. It can be assumed that also the municipal wastewater partial flow has inevitably come into contact with ozone. This contact takes place in the inlet pipe to the coarse material cell and also in the coarse material cell. The total contact time of the ozone with the wastewater flow is difficult to assess and, according to all known information, is about 15 to 20 s in the pipe to the coarse material cell and then in the coarse material cell at seconds to a few minutes, while the actual reaction time between ozone and wastewater constituents should be less. Sampling after the theoretical contact time for testing the immediate effect of ozone is unfortunately not possible due to the practical structure of the system.

The COD inlet and outlet values in relation to the mixed inlet with C-source are listed in the following Table 4.19. As a result of the fluctuations in the feed, somewhat

larger deviations in the discharge can also be found. For the same 5 measuring days an increase of the elimination rate of about 2% was achieved by the GAK filter.

MBR + Postozoning + GAK

During post-ozoning, ozone was added to the filtrate (MBR effluent) in the filtrate tank. The exact point of dosing is shown in Fig. 4.9. The aim was to decompose the inert COD or the COD not yet decomposed in the biological treatment stage into filterable “fragments” by ozonation. There may also be pharmaceutical and other trace substances in the plant effluent which can be destroyed by oxidation. The resulting “fragments” can then be filtered out through the GAK filter if necessary.

The contact time of the water with the ozone was on average about 5 min. The excess ozone was removed from the container via a vent pipe. Based on practical experience in Germany and China, different dosage quantities were tested, which varied between 3 and approx. 20 mg/l filtrate depending on the source of supply. Figure 4.26 shows the COD inflow and outflow values and the corresponding ozone quantity ($n = 8$, outflow values from different sampling points are also shown on a large scale).

It can be seen that the limit value of 50 mg/l can always be complied with. However, the COD discharge value cannot be reduced constantly by using post-ozoning alone. As with pre-ozoning, a significant increase in the ozone quantity does not result in a higher purification performance in terms of COD. In this case, the downstream GAK filter leads to the separation of a fairly large proportion of the remaining COD at an increased dosing quantity. On average, the use of the GAK filter reduces the incoming COD concentration of the already ozonated filtrate of the membrane stage by about 20%. The average COD elimination rate between the plant outlet not yet treated with ozone and the outlet after the GAK filter is even almost 30%. This is due to the fact that the ozone makes the inert COD portion filterable by splitting.

The average COD elimination levels, as well as inflows and outflows, are summarized in Table 4.20. It is clear that the effluent concentration can be further reduced with each stage - especially by combining it with the GAK filter. However, even here the number of measured data is not sufficient to draw a meaningful conclusion due to the limited test time.

MBR + PAK (+GAK)

In order to make more powerful statements about the effect of dosing PAHs on the cleaning performance of the test plant, an additional series of tests was carried out in which only PAHs were added to the plant as dosing agents. The results of the tests are presented in this chapter.

The PAH was dissolved in water (100 g/l) in a canister and added to the revitalisation by means of a peristaltic pump. The exact dosing point is shown in Fig. 4.9 or in the picture in the appendix. To prevent the PAHs from settling in the PAH solution, the solution was constantly mixed in the canister with the aid of aeration bars.

According to [15], to reduce the COD concentration from 50 mg COD/l to 20 mg COD/l, 20 mg PAH/l must be dosed. The average COD withdrawal in their investigations was 0.8–1.2 g COD/g PAH. Different dosages of PAH were investigated in

Fig. 4.26 Inflow and effluent concentrations of COD of the operating phase MBR + post-ozoning + GAK

the operating phase, varying between 10 and 50 mg/l. Figure 4.27 shows the COD inflow and outflow values and the dosing quantities of PAHs per litre of mixed feed ($n = 7$). The corresponding operating conditions are listed in the appendix.

Due to the time limit, only 2 to a maximum of 3 measuring days could be carried out for each dosing variant. During this operating phase, the plant was fed with PA batches that had already been subjected to the membrane stage and were presumably difficult to degrade. These batches are characterised by constantly low COD concentrations and poor BOD5:N ratios. It is noticeable that the significant increase in the PAH dosage did not lead to any improvement and that the limit value for COD of 50 mg/l in the filtrate could not be met on measurement day 80. However, the downstream GAK filter means that the limit value is undercut.

It can be assumed that trace substances that have accumulated on the large inner surface of the PAHs have been removed together with the PAHs with the ODP. However, the dry matter content of the sludge in the aeration tanks and the filter chamber has increased significantly (by approx. 5 g/l each) due to the use of

Fig. 4.27 COD inflow and outflow values of the operating phase MBR + PAH (+ GAK)

PAHs. The optimum values for the sludge parameters could therefore no longer be maintained for the short-term measures.

The following table lists all measured parameters in the mixed feed (with glucose) and the respective processes with the elimination rates. The lower purification performance for TP and TN compared to the FM operating phase indicates that PAH alone as an additional stage in combination with MBR cannot increase the plant performance in terms of nutrient elimination (Table 4.21).

In addition to the dosing of PAH, the pre-ozonation of the PA partial water stream was tested on one day and the post-ozonation of the MBR filtrate on one day. Since only one day was tested for each type of ozonation, no representative conclusions can be drawn from the results. It can be stated that no major COD cleaning performance was achieved by using both ozonation variants.

4.1.2.4.3 Comparison and Evaluation of Results

The results clearly show that the use of the GAK filter causes the most significant increase in COD cleaning performance. If we take COD measured values before and after the GAK filter every day, we obtain an average additional increase in the degree of elimination of approx. 20% ($n = 53$). This means that the COD discharge values can be reduced by about one fifth. This also includes all measurement days on which other processes were tested (ozonation, FM, FHM, PAH).

The results of the sole use of the test facility (MBR stage) and the combination of the MBR stage and the GAK filter ($n = 23$) are shown in the following figure in the form of box plots, so that strongly deviating values have less influence on the representation. This illustration also clarifies the statement that the cleaning performance can be increased by using GAK filters, as the median (the line dividing the box) of the “MBR + GAK” combination is 8 mg/l below the median of the MBR stage alone (Fig. 4.28).

To go into the COD elimination further, it can be stated that in addition to the use of the GAK filter, the use of other cleaning stages also produced good results.

Fig. 4.28 Boxplots for effluent concentrations of COD before and after GAK filtration

Unfortunately, it was not possible to collect a lot of data for some measurement series (ozonation, FM, PAH), so that the statements made on this should be confirmed in further tests. Due to the great variation in PA quality between different PA batches (see Fig. 4.18 and Fig. 4.19), a direct comparison of the absolute effluent concentrations of all test series is not of great importance. Nevertheless, the following diagram shows the average COD elimination levels of each test series. In order to be able to assess the significance of the results, the number of measured values for the respective test series is also given. The combination “FM + MBR + PAH + GAK” shows (for a small test series) the best elimination levels, which is probably due to the extremely high inlet concentrations. In case of very high COD inlet values, slight increases in the degrees of elimination cause big differences in the outlet values. This should be taken into account when planning new wastewater treatment plants in the region. It is noticeable that the treatment performance of the “MBR + PAH + GAK” test series is decreasing compared to others. Even with GAK, the average rate does not reach that of the “MBR” test series. The reason for this is, as already clarified, the commissioning of the membrane stage in NEPG, whose effluents from that time on contained hardly degradable COD and only had a negative dilution effect on the entire feed (Fig. 4.29).

Fig. 4.29 Mean COD elimination rates for the different pilot phases.

Table 4.16 Inflow and effluent concentrations and elimination rates of the operating phase MBR in T2

Parameters		Mixed feed [mg/l]		Outflow [mg/l]		Elimination rate [%]	
Description	n	Ø	s	Ø	s	Ø	s
COD	28	313,4	43,2	32,3	12,0	89,7%	4,6%
NH ₄ -N	26	23,7	5,6	0,10	0,04	99,6%	16,1%
TN	22	41,2	11,0	19,4	6,0	49,9%	14,8%
TP	20	2,9	0,4	0,54	0,2	81,3%	8,0%
SS	22	87,7	19,4	0,07	0,25	99,9%	0,2%

The results of the test series with ozonation had not shown in the relatively short test period that ozone can act more effectively than activated carbon for the treatment of the wastewater streams in Shenyang. For economic and safety reasons, activated carbon (in both forms) could be of more importance for large-scale industrial plants. In general, the pilot plant was able to eliminate at least 87% of the COD loads in the influent with a PA content of up to 30% under all possible process combinations. The limit value of 50 mg/l of the SK IA could be maintained on almost all measuring days even without GAK or other processes (but with C-dosage).

As can be seen from Table 4.16, the use of the pilot plant without any further processes has made it possible to achieve cleaning performances for COD, BOD₅, NH₄-N, TP and SS that meet the highest effluent standard IA from Table 4.2. For BOD, NH₄-N and SS, the standards are far below those shown in Table 4.2. The limit value of TP (0.50 mg/l) is only slightly exceeded (0.52 mg/l). For the TP effluent values, it should be noted that the use of FM has resulted in an increase in cleaning performance. The addition of FM did not result in significantly lower TP values. Here the cleaning performance is increased by just 1.45%. In general, it can be said that the use of FM is a possibility to further reduce both TP and COD effluent values (especially for inert COD contents). This can be seen in the test results presented as well as in the results from the preliminary tests for FM selection, where the use of the PAC has already achieved a COD elimination level of 20% and a TP elimination level >80%.

Only the limit value for TN cannot always be complied with and is exceeded by almost 30%. The reasons for this are, as explained several times, the oxygen carry-over from the filter chamber into the denitrification tank and the poor substrate supply in the inlet. In order to support the degradation of TN, glucose was added as a

Table 4.17 Mixed feed and effluent concentrations and elimination rates of COD for the operating phases MBR and MBR + GAK

Procedure		Mixed feed [mg/l]		Outflow [mg/l]		Elimination rate [%]	
Description	n	Ø	s	Ø	s	Ø	s
MBR	18	311,1	49,2	32,7	11,8	89,5%	3%
MBR + GAK	18	311,1	49,2	26,7	8,7	91,5%	2%

Table 4.18 Mixed feed and effluent concentrations and elimination rates for different parameters of the operating phase MBR + GAK

Parameters		Mixed feed [mg/l]		Outflow [mg/l]		Elimination rate [%]	
Description	n	Ø	s	Ø	s	Ø	s
COD	18	311,1	49,2	26,7	8,7	91,5%	2%
TN	3	42,83	8,0	20,20	0,9	50,1%	10,4%
TP	3	2,52	0,5	0,37	0,2	86,3%	7,3%
SS	18	72,63	39,2	0,00	0	100%	0

Table 4.19 Mixed feed and effluent concentrations and elimination rates of COD in the operation phase pre-ozonation + MBR + GAK

Procedure		Mixed feed [mg/l]		Outflow [mg/l]		Elimination rate [%]	
Description	n	Ø	s	Ø	s	Ø	s
Preozoning + MBR	7	343,8	87,1	33,0	11,5	89,7%	4,3%
Preozoning + MBR + GAK	5	370,1	90,5	25,6	10,6	92,7%	2,8%

Table 4.20 Mixed feed and effluent concentrations and elimination rates of COD for the operation phases MBR, MBR + post-ozoning and MBR + post-ozoning + GAK

Procedure		Mixed feed [mg/l]		Outflow [mg/l]		Elimination rate [%]	
Description	n	Ø	s	Ø	s	Ø	s
MBR	8	307,5	32,9	33,5	11,5	89,1%	3,7%
MBR + Postozoning	8			31,0	10,5	89,8%	3,6%
MBR + Postozoning + GAK	8			23,9	8,9	92,3	2,7%

Table 4.21 Mixed feed and effluent concentrations and elimination rates of COD, TN and TP for the operation phase MBR + PAH (+ GAK)

Procedure		Mixed feed [mg/l]		Outflow [mg/l]		Elimination rate [%]	
Description	n	Ø	s	Ø	s	Ø	s
COD	MBR + PAK	7	323,1	30,6	41,6	6,8	86,9%
	MBR + PAK + GAK	4	317,8	30,1	34,5	7,0	88,9%
TN	MBR + PAK	7	48,1	3,2	24,1	3,3	49,8%
TP	MBR + PAK	5	3,4	0,1	0,4	0,1	88,3%

C source to varying degrees (setting C:N ratio), which had a great effect to a certain extent. However, the TN feed values of the PA were subject to strong fluctuations, so that the adjustment of the dosing quantity could often only be carried out too late - as soon as the measured values were announced by the laboratory. Figure 4.30

Fig. 4.30 Composition of nitrogen in the PA over the entire project period

shows the measured nitrogen fractions in PA of all batches. Significant changes in composition are only seen from the start of operation of the membrane stage of NEPG with a dominance of nitrate and residual N, whereas before that there are strong fluctuations. The large proportion of organic residual N also confirms the poor degradability of TN in PA.

In order to investigate the effect of C-dosage or denitrification to a large extent, nitrite and nitrate concentrations were also measured in the effluent (filtrate) on certain days. Figure 4.31 shows that the nitrate fraction had been decomposed properly under C-dosage independent of test series and PA content, with nitrite and NH₄-N hardly being found. The dosing ratio (BOD₅: N 4–5) tested was sufficient to bring the nitrate concentration below 10 mg/l for most of the measuring days, even in the presence of oxygen carry-over. Not degradable are the residual N-fractions existing in the mixed feed, which are organic or inert and cannot be biologically ammoniated. For the elimination of this fraction further approaches are necessary.

Fig. 4.31 Composition of nitrogen in the effluent (filtrate) over the entire project period.

4.1.2.4.4 Recommendation for Action on Pharmaceutical Wastewater Treatment in Shenyang

The main objective of subproject T2 is to develop a recommendation for the treatment of pharmaceutical (and municipal) wastewater for the Shenyang region.

From a purely process-technical point of view, it can be interpreted from the test results that for a locally planned mixed treatment of different types of wastewater, in addition to the use of the membrane activated sludge process, above all the downstream connection of activated carbon filters is to be used. Not only COD effluent concentrations can be reduced in this way, but also trace material loads. The recommendation to use GAK filters can be supported by a large amount of data, in contrast to other test series.

The results of the test series on ozonation also provide high COD elimination rates. However, ozone is not easy to handle and the energy costs for ozone production in ozone generators are also high. The corrosive effect has already been shown after a few days in the test plant on the ozone system, when leaks occurred in connections and hoses. This leads to extensive maintenance work and associated costs. In addition, unwanted oxidation products can be produced during ozonation. In this case, precise investigations are necessary for concrete plant planning. It is estimated that the micro pollutants introduced in Germany a few years ago will not be regarded as standard parameters in China in the near future, so that the use of ozonation is not recommended as a first priority compared to GAK filters.

The dosing of external C-source can be used to adjust the C:N ratio at high TN feed values. Since the majority of the COD in pharmaceutical wastewater is most likely inert, dosing of readily degradable carbon in the form of glucose or similar will still be useful to support the degradation of TN and TP. However, the cost and effort factor must also be taken into account here. For example, intermittent dosing is recommended, which should be based on the results of preliminary tests and online monitoring of the COD and nitrate concentrations in the mixed feed or in the activated sludge.

The highest COD elimination rates were achieved by a combination of pre-precipitation of PA, treatment in the MBR pilot plant, dosing of PAH into the revitalisation system and downstream connection of a GAK filter. Due to the cost factor and the complexity of mixing and dosing, only one of the two dosing agents should be selected in large-scale technology (and if necessary only for emergencies). It should be noted that PAH can be dosed in powder form. As in subproject T2, preliminary tests are useful for selecting a suitable agent. For the pharmaceutical wastewater of NEPG in Shenyang, the use of flocculants can be dispensed with, since no or only low elimination rates were achieved (COD: no increase; TP: 1.45%).

According to the collected and analysed results, the combination of a possible pre-precipitation for heavily loaded wastewater substreams (especially with high COD and TP inflow values with online monitoring as a prerequisite), a possible simultaneous precipitation as well as glucose dosage into the activation, the membrane activated sludge process as main component and a downstream activated carbon filter is proposed as a recommendation for the co-treatment of pharmaceutical wastewater in municipal wastewater treatment plants in Shenyang.

Fig. 4.32 Schematic diagram of the NEPG wastewater treatment plant

As a concrete example of the technical upgrade of an industrial wastewater treatment plant, the NEPG wastewater treatment plant, after an external membrane module has already been installed, can be further modified by treatment with FM and the use of activated carbon filters in case of emergency. After thorough preliminary investigations, ozonation or PAH dosage can also be carried out in an emergency. The technical and economic feasibility must be checked in the course of this and further investigations and tests must be carried out with the actual wastewater. Fig. 4.32 shows a schematic diagram of the NEPG's operational wastewater treatment plant with the technical equipment (fields marked green).

Obviously, there is a great variation in the material loads of the delivered wastewater batches of NEPG, which can be traced back to both the functioning of the operational pre-treatment stages and the production of NEPG. Throughout the entire project period, different production processes were running in the pharmaceutical plant, the cycle of which is unknown for reasons of confidentiality. The fluctuations are not only to be found in NEPG, but also in experience with other plants that have no pre-treatment or only limited pre-treatment. Therefore, beyond the procedural recommendations for action, stricter controls of the discharging industrial plants as well as the technical upgrading of the operational wastewater treatment plants should be addressed in order to ensure that the set discharge standards into the sewerage system (see Table 4.5) can be met.

However, as can be seen from the results (also from T1), a large amount of inert COD is discharged into the public sewerage system by NEPG or other companies. The inert COD cannot be biodegraded at all or only to a small extent. Furthermore, the nutrient ratio in industrial wastewater is not suitable for the degradation of nitrogen, a typical example being the extremely poor C:N ratio in pharmaceutical wastewater after the use of NEPG's own membrane stage. The cleaning performance of the public sewage treatment plant is impaired by the dilution effect of industrial partial flows, even though the discharge standard of the indirect dischargers is maintained.

In this context, it is particularly recommended to adapt the Chinese discharge standard of plants where not only limit concentrations for certain parameters have

to be observed. The discharging companies should ensure a nutrient ratio in their already pre-treated wastewater by adapting the process technology so that municipal wastewater treatment plants have better basic conditions for nitrogen and phosphorus degradation. Further nutrient elimination in industrial wastewater.

4.1.4 Annex

sampling protocol pilot plant Shenyang							
sampler: Maximilian Rolf		date: 24.11.17		320			
weather: sunny		flow MBR (l/h)					
sampling location	municipal intake	drain without ozone	nitrification	filter chamber	drain after ACF	pharma intake	
sampling type	spot check	mixed check	spot check	spot check	spot check	spot check	
time	08:55	9:00, 13:00, 15:00		09:10	09:05	15:10	15:30
on-side parameters							
temperature (°C)	14,9	17,5; 18,0; 16,3					26,5
PH value	7,65	7,77					7,63
conductivity	1581	1397					1797
oxygen content							0,16
visual coloring	light grey	clear	dark brown	dark brown	clear	grey	
cloudiness	heavy	none	heavy	heavy	none	heavy	
smell	putry, jauchy, sweet	lightly earthy	earthy	earthy	lightly earthy	putry (rotten eggs)	
Pretreatment		cooled			cooled	cooled	
examined parameters							
COD(mg/L)	198	20			20	182	
glc.COD(mg/L)							
BOD5(mg/L)							
NH4-N(mg/L)	22,75	0,12					43
NO3(mg/L)	28,4	10,8					52
PO4(mg/L)	2,77	0,08					2,93
TK(N)							0,1027
gTr(%)							0,0355
SS	128	1					84
TS(mg/L)			9624	12344			
SV30(ml/L)			1000	1100			
comment							after 15.30 2% Lower than 1000000 tank every 120 min

Annex 4-1: Sampling protocol

Annex 4-2: Dosing tank for glucose and powdered activated carbon (top left), dosing hose (bottom left) and view into the experimental container

Annex 4-3: ozonegenerator „C-Lasky DTI“ by „AirTree“ (FiW)

Annex 4-4: flocculation tank (inside) and agitator (FiW)

Annex 4-5: adjustable operating parameters inclunding scale

Pre-cleaning	Finescreen	Feeding pump 1	Stop	Auto	By hand
		drive Finescreen	Stop	Auto	By hand
		Dry running	0 – 100 %		
		Rake off	0 – 100 %		
		Rake on	0 – 100 %		
		High alarm	0 – 100 %		
		Delay time	0 – 999 s		
		Pace on	0 – 999 s		
		Pace off	0 – 999 s		
		Max. runtime	0 – 999 h		
	pharmaceutical waste-water	Pharma transferring pump	Stop	Auto	By hand
		Dosing pump FM	Stop	Auto	By hand
		runtime FM-pump	0 – ∞ s		
		Dosing pump FHM	Stop	Auto	By hand

		Runtime FHM pump	0 - ∞ s		
		Agitator	Stop	Auto	By hand
		Mixing time	0 – 999 h		
		Feeding pump 2	Stop	Auto	By hand
		Dry running	0 – 100 %		
		Pump off	0 – 100 %		
		Start of flucculation	0 – 100 %		
		High alarm	0 – 100 %		
		NOR feeding pump 2	0 – 100 %		
		Total time	0 – 999 min		
Activation	Denitrification	Compressor denitrification	Stop	Auto	By hand
		Pace on	0 – 999 s		
		Pace off	0 – 999 s		
	Nitrification	Compressor nitrification	Stop	Auto	By hand
		Pace on	0 – 999 s		
		Pace off	0 – 999 s		
		Min air flow	0 – 99 Nm ³ /h		
		Max air flow	0 – 99 Nm ³ /h		
	Activation tank	Dry running	0 – 100 %		
		Filtration off	0 – 100 %		
		Filtration in	0 – 100 %		
		Feeding pump 1 stop	0 – 100 %		
		Feeding pump 2 stop	0 – 100 %		
		High alaerm	0 – 100 %		
	Ball valves	Recirculationpump	Stop	Auto	By hand
		EKH M10	Stop	Auto	By hand
		EKH M11	Stop	Auto	By hand
Filtration	Compressor filtration	Compressor 1 filtration tank	Stop	Auto	By hand
		Compressor 2 filtration tank	Stop	Auto	By hand
		Pace on	0 – 999 s		
		Pace off	0 – 999 s		
		Min air flow	0 – 99 Nm ³ /h		
		Max air flow	0 – 99 Nm ³ /h		
	Filtration	Filtrate pump	Stop	Auto	By hand
		Dry running	0 – 100 %		
		Filtrate amount	0 – 3000 L/h		
		Filtrate amount min.	0 – 3000 L/h		
		p_min	0 – (-350) mbar		
		p_minmin	0 – (-350) mbar		
		Pace on	0 – 999 s		

discharge and regulation	Filtrat tank	Pace off	0 – 999 s		
		Manual set point	0 – 100%		
		Filtrate transfer pump	Stop	Auto	By hand
		Pump off	0 – 100 %		
		Pump on	0 – 100 %		
		High alarm	0 – 100 %		
	Sludge discharge	Setpoint sludge discharge	0 – 100 m ³		
		Actual value sludge discharge	-		
		Parts sludge	0 – 5 %		
	Coarse	Setpoint coarse-discharge	0 – 200 m ³		
		Actual value coarse-discharge	-		
		Chemical cleaning	on	off	

Annex 4-6: Used sensors and probes and their tasks

Sensor/Probe	Installation point	Purpose
Level sensor	Coarse material cell, nitrification / denitrification basin, filter chamber	Operational flow
Temperature sensor	Nitrification / denitrification basins	Biodegradation monitoring
Oxygen content probe	Nitrification basin	Assessment of the ventilation setting
Redox potential probe	Denitrification basin	Assessment of denitrification performance
Pressure sensor	Between the diaphragm and the diaphragm pump	Monitoring the condition of the membrane

Annex 4-7: Volume of the plant components of the test plant

Investment component	Description	Average filling level	Volume	Efficient Volume
Filter chamber	V_F	91%	2 m ³ — 0,8 m ³	1,2 m ³
Aeration tank (denitrification: nitrification)	V_{BB} ($V_{Deni.}:V_{Nltri.}$)	67% - 75%	1,4 m ³ (1:1)	1 m ³
Coarse matter cell	V_G	100%	approx. 0,8 m ³	0,8 m ³
Activated carbon filter	V_{AKF}	-	31,3 L each	1,3 L each
Filtrate tank	V_P	50%	approx. 60 L	approx. 60 L
Pipes (length: 30 m)	V_R	-	approx. 60 L	approx. 60 L

Determination SV30

First the stand cylinder is filled with 800 ml MBR wastewater (process water). Then the sample to be tested is removed from the filter chamber or nitrification basin. Before

the sample can be taken from the nitrification, the aeration of the nitrification must be switched on for 2 min to ensure that the nitrification sludge is mixed. Afterwards, the cylinder is filled up with 200 ml sludge, so that the volume of the filtrate-sludge-mixture is 1 L. By closing the cylinder and the subsequent mixing by shaking, a complete mixing in the cylinder is achieved. Now a 30-min settling time is waited for. The sludge should now have settled so that a clear and a sludgy phase can be clearly seen. The read value of the sludge phase (in ml) must now be multiplied by 5 to obtain the SV30.

Annex 4-8: Allocation of the calendar dates to the diagram numbers for project phase T1

Nr.	date	Nr.	date	Nr.	date	Nr.	date
1	04.08.2017	32	04.09.2017	63	05.10.2017	94	05.11.2017
2	05.08.2017	33	05.09.2017	64	06.10.2017	95	06.11.2017
3	06.08.2017	34	06.09.2017	65	07.10.2017	96	07.11.2017
4	07.08.2017	35	07.09.2017	66	08.10.2017	97	08.11.2017
5	08.08.2017	36	08.09.2017	67	09.10.2017	98	09.11.2017
6	09.08.2017	37	09.09.2017	68	10.10.2017	99	10.11.2017
7	10.08.2017	38	10.09.2017	69	11.10.2017	100	11.11.2017
8	11.08.2017	39	11.09.2017	70	12.10.2017	101	12.11.2017
9	12.08.2017	40	12.09.2017	71	13.10.2017	102	13.11.2017
10	13.08.2017	41	13.09.2017	72	14.10.2017	103	14.11.2017
11	14.08.2017	42	14.09.2017	73	15.10.2017	104	15.11.2017
12	15.08.2017	43	15.09.2017	74	16.10.2017	105	16.11.2017
13	16.08.2017	44	16.09.2017	75	17.10.2017	106	17.11.2017
14	17.08.2017	45	17.09.2017	76	18.10.2017	107	18.11.2017
15	18.08.2017	46	18.09.2017	77	19.10.2017	108	19.11.2017
16	19.08.2017	47	19.09.2017	78	20.10.2017	109	20.11.2017
17	20.08.2017	48	20.09.2017	79	21.10.2017	110	21.11.2017
18	21.08.2017	49	21.09.2017	80	22.10.2017	111	22.11.2017
19	22.08.2017	50	22.09.2017	81	23.10.2017	112	23.11.2017
20	23.08.2017	51	23.09.2017	82	24.10.2017	113	09.01.2018
21	24.08.2017	52	24.09.2017	83	25.10.2017	114	10.01.2018

22	25.08.2017	53	25.09.2017	84	26.10.2017	115	11.01.2018
23	26.08.2017	54	26.09.2017	85	27.10.2017	116	12.01.2018
24	27.08.2017	55	27.09.2017	86	28.10.2017	117	13.01.2018
25	28.08.2017	56	28.09.2017	87	29.10.2017	118	14.01.2018
26	29.08.2017	57	29.09.2017	88	30.10.2017	119	19.02.2018
27	30.08.2017	58	30.09.2017	89	31.10.2017	120	20.02.2018
28	31.08.2017	59	01.10.2017	90	01.11.2017	121	21.02.2018
29	01.09.2017	60	02.10.2017	91	02.11.2017	122	22.02.2018
30	02.09.2017	61	03.10.2017	92	03.11.2017	123	23.02.2018
31	03.09.2017	62	04.10.2017	93	04.11.2017		

Annex 4-9: Allocation of the calendar dates to the diagram numbers for project phase T2

1	24.11.17	23	16.12.17	45	07.01.18	67	04.02.18
2	25.11.17	24	17.12.17	46	08.01.18	68	05.02.18
3	26.11.17	25	18.12.17	47	15.01.18	69	06.02.18
4	27.11.17	26	19.12.17	48	16.01.18	70	07.02.18
5	28.11.17	27	20.12.17	49	17.01.18	71	08.02.18
6	29.11.17	28	21.12.17	50	18.01.18	72	09.02.18
7	30.11.17	29	22.12.17	51	19.01.18	73	10.02.18
8	01.12.17	30	23.12.17	52	20.01.18	74	11.02.18
9	02.12.17	31	24.12.17	53	21.01.18	75	12.02.18
10	03.12.17	32	25.12.17	54	22.01.18	76	13.02.18
11	04.12.17	33	26.12.17	55	23.01.18	77	14.02.18
12	05.12.17	34	27.12.17	56	24.01.18	78	24.02.18
13	06.12.17	35	28.12.17	57	25.01.18	79	25.02.18
14	07.12.17	36	29.12.17	58	26.01.18	80	26.02.18
15	08.12.17	37	30.12.17	59	27.01.18	81	27.02.18
16	09.12.17	38	31.12.17	60	28.01.18	82	28.02.18
17	10.12.17	38	01.01.18	61	29.01.18	83	01.03.18
18	11.12.17	40	02.01.18	62	30.01.18	84	02.03.18
19	12.12.17	41	03.01.18	63	31.01.18	85	05.03.18
20	13.12.17	42	04.01.18	64	01.02.18	86	06.03.18
21	14.12.17	43	05.01.18	65	02.02.18	87	07.03.18
22	15.12.17	44	06.01.18	66	03.02.18	88	08.03.18

Annex 4-10: Data of the siClaro® FM 622 and the MBR (MMS, o. J.)

	siClaro® FM 622	MBR
Filtration area	25 m ²	50 m ²
Dimensions (L x W x H)	608 x 362 x 1360 [mm]	2 Modules of this size
max. flowrate	11 l/(m ² *h)	22 l/(m ² *h)
max. flow	14,700 m ³ /d	29,400 m ³ /d
max. Membrane pressure	-300 mbar	-300 mbar
Purge air requirement	16,500 Nm ³ /h	33,000 Nm ³ /h

Annex 4-11: Operating conditions and operating parameters for all T2-related test phases

Operating phase MBR

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age [d]</i>	34	20,56	2,58
Q _N [l/h]	34	292,61	57,34	TS _{BB} [g/l]	34	11,98	1,65
Q _B [l/h]	34	365,76	71,67	SV30 _{BB} [ml/l]	34	1026	125
MF _N [l/(m ² *h)]	34	6,06	1,10	B _{R,COD} [kg/(m ³ *d)]	34	1,10	0,27
MF _B [l/(m ² *h)]	34	7,57	1,38	B _{R,BOD5} [kg/(m ³ *d)]	34	0,59	0,21
P _N [l/(m ² *h*bar)]	34	69,86	23,04	B _{TS,COD} [kg/(kg _{TS} *d)]	34	0,088	0,044
P _B [l/(m ² *h*bar)]	34	87,32	28,80	B _{TS,BOD5} [kg/(kg _{TS} *d)]	34	0,048	0,025
pH	34	7,52	1,19	COD:N	34	3,83	1,69
O ₂ [mg/l]	34	2,18	0,55	(COD:N) _G	34	7,65	2,12
T _{BB} [°C]	30	18,48	0,90	BOD ₅ :N	34	1,35	0,96
RV	34	6,18	1,86	(BOD ₅ :N) _G	34	4,33	1,43

MBR + GAK

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age [d]</i>	23	22,14	3,11
Q _N [l/h]	23	296,81	62,66	TS _{BB} [g/l]	23	11,97	1,79
Q _B [l/h]	23	371,01	78,33	SV30 _{BB} [ml/l]	23	1026	125
MF _N [l/(m ² *h)]	23	6,15	1,12	B _{R,COD} [kg/(m ³ *d)]	23	1,15	0,27
MF _B [l/(m ² *h)]	23	7,68	1,40	B _{R,BOD5} [kg/(m ³ *d)]	23	0,65	0,22
P _N [l/(m ² *h*bar)]	23	72,28	25,96	B _{TS,COD} [kg/(kg _{TS} *d)]	23	0,086	0,030
P _B [l/(m ² *h*bar)]	23	90,35	32,45	B _{TS,BOD5} [kg/(kg _{TS} *d)]	23	0,049	0,019
pH	23	7,44	1,43	COD:N	23	3,75	1,90
O ₂ [mg/l]	23	2,21	0,55	(COD:N) _G	23	7,75	2,29
T _{BB} [°C]	19	18,54	0,76	BOD ₅ :N	23	1,39	0,83
RV	23	7,14	1,65	(BOD ₅ :N) _G	23	4,49	1,32

Preozoning + MBR + GAK

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age [d]</i>	7	26,84	3,01
Q _N [l/h]	7	239,74	45,89	TS _{BB} [g/l]	7	12,65	0,91
Q _B [l/h]	7	299,68	57,37	SV30 _{BB} [ml/l]	7	1021	99
MF _N [l/(m ² *h)]	7	4,86	0,99	B _{R,COD} [kg/(m ³ *d)]	7	0,97	0,41
MF _B [l/(m ² *h)]	7	6,07	1,24	B _{R,BOD5} [kg/(m ³ *d)]	7	0,45	0,25

P_N [l/(m ² *h*bar)]	7	64,01	18,78	$B_{TS,COD}$ [kg/(kg _{TS} *d)]	7	0,074	0,037
P_B [l/(m ² *h*bar)]	7	80,01	23,47	$B_{TS,BOD5}$ [kg/(kg _{TS} *d)]	7	0,034	0,022
pH	7	7,70	0,22	COD:N	7	6,36	2,88
O ₂ [mg/l]	7	1,61	0,54	(COD:N) _G	7	10,48	3,67
T _{BB} [°C]	7	19,01	1,24	BOD ₅ :N	7	2,21	1,78
RV	7	6,46	2,69	(BOD ₅ :N) _G	7	5,40	2,35

MBR + postozoning + GAK

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age</i> [d]	8	23,39	3,53
Q_N [l/h]	8	273,34	42,76	TS _{BB} [g/l]	8	12,07	1,42
Q_B [l/h]	8	341,67	53,45	SV30 _{BB} [ml/l]	8	1044	136
MF _N [l/(m ² *h)]	8	5,56	0,92	B _{R,COD} [kg/(m ³ *d)]	8	0,93	0,19
MF _B [l/(m ² *h)]	8	6,95	1,15	B _{R,BOD5} [kg/(m ³ *d)]	8	0,45	0,15
P_N [l/(m ² *h*bar)]	8	67,54	13,95	$B_{TS,COD}$ [kg/(kg _{TS} *d)]	8	0,073	0,023
P_B [l/(m ² *h*bar)]	8	84,42	17,44	$B_{TS,BOD5}$ [kg/(kg _{TS} *d)]	8	0,036	0,016
pH	8	7,73	0,14	COD:N	8	3,85	1,01
O ₂ [mg/l]	8	2,29	0,49	(COD:N) _G	8	7,37	1,57
T _{BB} [°C]	8	18,1	1,05	BOD ₅ :N	8	1,28	0,43
RV	8	7,1	2,38	(BOD ₅ :N) _G	8	4,05	0,96

FM (+ FHM) + MBR (+ PAK) (+ GAK)

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age</i> [d]	15	24,11	2,30
Q_N [l/h]	15	265,73	40,27	TS _{BB} [g/l]	13	14,29	1,99
Q_B [l/h]	15	332,16	50,34	SV30 _{BB} [ml/l]	12	1160	164
MF _N [l/(m ² *h)]	15	5,43	0,87	B _{R,COD} [kg/(m ³ *d)]	15	1,95	0,84
MF _B [l/(m ² *h)]	15	6,79	1,09	B _{R,BOD5} [kg/(m ³ *d)]	15	0,72	0,32
P_N [l/(m ² *h*bar)]	15	52,80	8,73	$B_{TS,COD}$ [kg/(kg _{TS} *d)]	13	0,150	0,101
P_B [l/(m ² *h*bar)]	15	65,99	10,91	$B_{TS,BOD5}$ [kg/(kg _{TS} *d)]	13	0,055	0,033
pH	15	7,51	0,67	COD:N	15	9,38	3,45
O ₂ [mg/l]	15	2,15	0,58	(COD:N) _G	15	13,01	3,30
T _{BB} [°C]	12	19,77	0,50	BOD ₅ :N	15	1,99	1,23
RV	15	8,77	1,65	(BOD ₅ :N) _G	15	4,78	0,96

MBR + PAK (+ GAK)

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age</i> [d]	7	21,03	0,19
Q_N [l/h]	7	296,52	2,72	TS _{BB} [g/l]	7	13,75	1,07
Q_B [l/h]	7	370,65	3,40	SV30 _{BB} [ml/l]	7	964	35
MF _N [l/(m ² *h)]	7	6,00	0,85	B _{R,COD} [kg/(m ³ *d)]	7	1,04	0,10
MF _B [l/(m ² *h)]	7	7,50	0,92	B _{R,BOD5} [kg/(m ³ *d)]	7	0,46	0,05
P_N [l/(m ² *h*bar)]	7	63,97	9,79	$B_{TS,COD}$ [kg/(kg _{TS} *d)]	7	0,071	0,010

P_B [l/(m ² ·h·bar)]	7	79,96	12,24	B_{TS,BOD5} [kg/(kg _{TS} ·d)]	7	0,032	0,005
pH	7	8,01	0,16	COD:N	7	3,09	0,59
O₂ [mg/l]	7	2,16	0,53	(COD:N)_G	7	6,74	0,70
T_{BB} [°C]	7	19,23	0,89	BOD₅:N	7	1,02	0,13
RV	7	5,46	0,05	(BOD₅:N)_G	7	3,93	0,48

Supplementary trial phase T1: MBR + FM

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age</i> [d]	5	21,50	1,58
Q_N [l/h]	5	241,36	8,2	TS_{BB} [g/l]	5	15,81	0,55
Q_B [l/h]	5	301,7	10,20	SV30_{BB} [ml/l]	5	1250	96
MF_N [l/(m ² ·h)]	5	4,83	0,8	B_{R,COD} [kg/(m ³ ·d)]	5	0,98	0,1
MF_B [l/(m ² ·h)]	5	6,03	0,9	B_{R,BOD5} [kg/(m ³ ·d)]	5	0,39	0,05
P_N [l/(m ² ·h·bar)]	5	44,66	4,32	B_{TS,COD} [kg/(kg _{TS} ·d)]	5	0,06	0,005
P_B [l/(m ² ·h·bar)]	5	55,83	5,4	B_{TS,BOD5} [kg/(kg _{TS} ·d)]	5	0,02	0,005
pH	5	7,56	0,51	COD:N	5	6,00	1,32
O₂ [mg/l]	5	2,25	0,30	(COD:N)_G	5	11,74	1,64
T_{BB} [°C]	5	16,88	0,62	BOD₅:N	5	2,65	0,93
RV	5	5,81	0,2	(BOD₅:N)_G	5	7,15	0,97

Supplementary trial phase T1: MBR + PAK

<i>Operating parameters</i>	<i>n</i>	<i>average</i>	<i>s</i>	<i>Mud age</i> [d]	5	22,0	1,35
Q_N [l/h]	5	342,41	47,5	TS_{BB} [g/l]	5	13,40	0,51
Q_B [l/h]	5	428,01	59,3	SV30_{BB} [ml/l]	5	1000	0
MF_N [l/(m ² ·h)]	5	6,84	1,25	B_{R,COD} [kg/(m ³ ·d)]	5	1,04	0,10
MF_B [l/(m ² ·h)]	5	8,56	1,35	B_{R,BOD5} [kg/(m ³ ·d)]	5	0,62	0,09
P_N [l/(m ² ·h·bar)]	5	53,97	13,59	B_{TS,COD} [kg/(kg _{TS} ·d)]	5	0,07	0,006
P_B [l/(m ² ·h·bar)]	5	67,46	16,99	B_{TS,BOD5} [kg/(kg _{TS} ·d)]	5	0,04	0,006
pH	5	7,67	0,24	COD:N	5	5,37	1,24
O₂ [mg/l]	5	2,28	0,54	(COD:N)_G	5	11,14	1,17
T_{BB} [°C]	5	16,78	0,80	BOD₅:N	5	2,09	0,56
RV	5	4,98	0,67	(BOD₅:N)_G	5	6,64	0,33

References

1. Baumgarten S (2007) Membranbioreaktoren zur industriellen Abwasserreinigung, Dissertation zur Erlangung des akademischen Grades eines Doktors der Ingenieurwissenschaften von der Fakultät für Bauingenieurwesen der Rheinisch-Westfälischen Technischen Hochschule Aachen

2. Dohmann M, Buer T, Vossenkaul K (2002) Stand und weitere Entwicklung membrantechnischer Anlagen im Bereich der Wasserversorgung und Abwasserentsorgung. Vortrag, Büchel, Januar 2002

3. DWA 131 (2016) Arbeitsblatt DWA-A 131- DWA-Regelwerk Bemessung von einstufigen Belebungsanlagen, Hennef

4. DWA-M 22738 (2011) DWA-Merkblatt 227, Membran-Bioreaktor-Verfahren (MBR-Verfahren), DWA Fachausschuss KA 7, Hennef, Entwurf, Stand 27.07.2011
5. FiW eV (2015) SINOWASSER Vorhabensbeschreibung.
6. Hu P (2017) Nachhaltige Klärschlamm Entsorgungskonzepte für die Stadt Shenyang unter besonderer Berücksichtigung deutscher Erfahrungen, Masterarbeit am Lehrstuhl für Siedlungswasser- und Siedlungsabfallwirtschaft RWTH-Aachen
7. Itokawa H, Thiemig C, Pinnekamp J (2008) Design and Operating Experiences of Municipal MBR in Europe. *Water Sci Technol* 58(12):2319–2327
8. Jin L, Zhang G, Tian H (2014) Current state of sewage treatment in China. In: *Water Research*. 66 Jg., S. 85–98
9. Judd S (2011) *The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment*, Butterworth-Heinemann, second edition
10. Krause S, Zimmermann B, Thiemig C (2011) Untersuchungen zum ressourcenschonenden Betrieb von Membranbelebungsanlagen - Optimierungen hinsichtlich Energie- und Chemikalienbedarf, *Korrespondenz Abwasser* (58) Nr. 9, 2011
11. Li X, Li G (2015) A Review: Pharmaceutical Wastewater Treatment Technology and Research in China. In: *Asia-Pacific Energy Equipment Engineering Research Conference*. Zhuhai, China, 13–14 Juni 2015
12. MEP (2010) China environmental statistics annual report 2010, Ministry of Environmental Protection of the People's Republic of China
13. MEP (2016) China environmental statistics annual report 2016, Ministry of environmental protection of the People's Republic of China
14. Meteoblue AG (2018) Klima Shenyang 2018. https://www.meteoblue.com/de/wetter/vorher-sage/modelclimate/shenyang_china_2034937, zuletzt abgerufen am 23.05.2018
15. Metzger S, Kapp H (2007) Adsorptive Abwasserreinigung zur Verbesserung der Gewässerqualität, Hochschule Biberach, Institut für Geo- und Umwelt, Lehrgebiet und Labor für Siedlungswasserwirtschaft, 15 S.
16. Mitschke M (2013) Untersuchungen zur aeroben Abwasserreinigung ohne biologische Überschussschlammproduktion. (Technik). Hamburg: Diplomarbeiten Agentur
17. NEPG: Website der Northeast Pharmaceutical Group Co., Ltd. <http://www.nepharm.com>, zuletzt abgerufen am 16.01.2018
18. Pinnekamp J, Benström F, Nahrstedt A, Böhler M, Knopp G, Montag D, Siegerist H (2016) Leistungsfähigkeit granulierter Aktivkohle zur Entfernung organischer Spurenstoffe aus Abläufen kommunaler Kläranlagen. Ein Review halb- und großtechnischer Untersuchungen. Teil 1: Veranlassung, Zielsetzung und Grundlagen. In: *Korrespondenz Abwasser*. Jg. 63, 2016, Nr. 4, S. 276–289
19. Pinnekamp J, Friedrich H (2006) *Membrantechnik für die Abwasserreinigung*, Schriftenreihe Siedlungswasser- und Siedlungsabfallwirtschaft NRW, Band 1, 2. aktual. Aufl., FiW-Verlag, Aachen
20. Shan L (2017) Application and Demonstration of sewage treatment and sludge disposal technology in Shenyang. Vortrag des Shenyang Academy of Environmental Sciences, SINOWATER-Symposium 2017, Peking
21. Shenyang EPB (2017) Offizielle Homepage des Environmental Protection Bureau von der Stadt Shenyang. <http://www.syepb.gov.cn/data>, zuletzt abgerufen am 16.05.2018
22. Tian Z (2017) Upgrading Strategy of North WWT in Shenyang, Vortrag des Urban Water Environmental Department of CRAES, SINOWATER-Symposium 2017, Peking
23. Xiang L (2017) Treatment Technology of Pharmaceutical Wastewater. Vortrag des Chinese Research Academy of Environmental Sciences, SINOWATER-Symposium 2017, Peking
24. Xiao S, Zhang G (2011) Treatment of Berberine Pharmaceutical Wastewater Containing Copper by Bipolar Electrochemical Process. In: *Environmental Engineering Technology*. Jg. 1, 2011, Nr. 1, S. 295–299
25. Yun Y (2018) Upgrading of wastewater treatment plants in Germany and in China - progress and trend, a contribution to the closing Symposium Integrated Lake Basin Management Dianchi, Vortrag des Forschungsinstitut für Wasser- und Abfallwirtschaft an der RWTH Aachen (FiW) e.V., SINOWATER-Abschluss-symposium 2018, Kunming

26. Zhang P (2006) 沈阳铁西工业区改造的制度与文化因素 *Human Geograph*, vol. 21, No. 2, 04.2006
27. Zeng P, Du J, Liu Y, Gao H, Liu R, Song Y (2015) Pharmaceutical wastewater treatment in China and the world. A bibliometric analysis of research output during 1990–2013. *Res. Rev. J. Pharmaceutical Qual. Assurance. Jg. 1*, 2015, Nr. 1, S. 30–37

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